A Study into the Ultrasonic Cleaning of Wool

by

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Candidate’s Declaration

I certify that the thesis entitled: A Study into the Ultrasonic Cleaning of Wool submitted for the degree of Doctor of Philosophy

is the result of my own research and that where reference is made to the work of others, due acknowledgement is given.

I also certify that any material in the thesis which has been accepted for a degree or diploma by any university or institution is identified in the text.

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Abstract

The cleaning of wool is energy, time and resource intensive and produces large amounts of waste water with high chemical and biological oxygen demand. Cleaning occurs in a variety of ways at a number of different times during the production and use of a wool textile. Most cleaning processes impact the quality of wool fabric by causing felting shrinkage particularly for fine wool. The use of ultrasound during wool cleaning is a way of reducing the ecological and quality impacts that cleaning has on wool. Ultrasound is an efficient mass transfer mechanism that can improve contaminant removal while reducing the aggressive movement of liquor in the cleaning bath which may cause the entanglement of wool fibres.

This research investigates if the use of ultrasonic irradiation within a bath of water, wool and detergent can improve wool cleaning and enable the use of lower cleaning temperatures and less detergent. It examines the effect that ultrasonic irradiation has on the structure and properties of wool fibres and the properties of fabrics made from these fibres. Wool fibre scouring, ultrasonic fabric laundering, ultrasonic effects on single fibre properties and ultrasonically assisted wool dyeing were investigated.

An investigation into scouring optimisation with ultrasound was conducted on a five bath scouring process with three minute residence time per bath. Experiments showed that both scouring bath temperature and detergent concentration could be reduced while still maintaining a good cleaning efficiency. Fibre length after carding measurements established that the use of
ultrasonic irradiation for mass transfer within the scouring bath produced less fibre entanglement than traditional rake scouring. Wool fibres were found to absorb ultrasonic irradiation, but efficient scouring was achieved for fibre to liquor ratios up to 8.3 g/l.

An investigation into repeated ultrasonic wash cycles followed by drying to simulate repeated fabric laundering found that there was less fabric felting shrinkage and thickness change when compared with hand washing. The repeated cycles of ultrasound had no adverse effects on colour or fabric tensile strength. Cleaning of a stained fabric was conducted to determine if ultrasound assisted in the removal of stains. Common stains like hot coffee, hot tea, red wine, orange carbonated sugar drink and engine oil were allowed to stain a fabric for 24 hours before cleaning. Colour measurement of the stain before and after cleaning revealed that ultrasonics provided better stain release and removal for all stain types using both alkaline and acidic detergents. Martindale abrasion and ICI pilling measurement of fabrics after prolonged exposure to ultrasound in an acidic, neutral or alkaline cleaning bath showed that both pilling and abrasion resistance were unaffected by ultrasound exposure.

Microscopy studies of wool fibres that had undergone low and high intensity ultrasonic irradiation in a range of different treatment liquors revealed that the ultrasonic induced changes to fibre cuticle structure were dependent on the level of wetting of a fibre. Treatment in water only left a cushion of air on the surface or within the fibre that limited the impact of cavitation to a mild cracking of the cuticle. Thorough wetting in the presence of a detergent and an
alkali caused peeling and removal of part or all of the cuticle scales. The measurement of single fibre properties showed that low power ultrasound induced cuticle changes had no significant effect on fibre tensile strength and bending abrasion resistance.

An investigation into the effect that cuticle structure changes played on wool dyeing found that the rate of dye uptake was increased by pre-treatment with ultrasound. The numbers of pathways for dye to enter the fibre at low temperatures were increased and more pathways were provided when the sample was irradiated in a detergent and alkali than in water alone. Dyeing rate improvements due to dyeing in the presence of ultrasound were assisted by the ultrasound induced fibre cuticle changes.

Ultrasonic irradiation during wool cleaning has a significant benefit to the environment as it can reduce the energy inputs into cleaning, significantly reduce the detergent required for cleaning and reduce the level of detergent in waste water from cleaning. The use of ultrasonic irradiation as a replacement for mechanical agitation in a cleaning process reduces the level of irreversible fibre entanglement while still maintaining or improving the level of cleaning seen with the mechanical agitation. Ultrasonic irradiation in an aqueous environment can cause a change in the cuticle structure of the fibre, increasing the dyeing rate without significantly impacting on the fibre mechanical properties.
Introduction

At multiple stages during the life cycle of a wool textile it will need cleaning. Raw wool is contaminated by dust and dirt from the farm along with sweat (suint) and wool grease from the animal. These contaminants must be removed before efficient yarn production can occur. In use, wool textiles become contaminated with dust, dirt, food, grease, oils, body fluids, smells and other contaminants too numerous to list. These contaminants must be efficiently removed otherwise the garment is no longer fit for purpose.

The process of cleaning textiles and fibres is energy, time and resource intensive and produces large amounts of waste water with high chemical and biological oxygen demand. Most cleaning processes impact the quality of wool fabric by causing felting shrinkage. The use of ultrasound during wool cleaning is a way of reducing the ecological and quality impacts of cleaning. Ultrasound is an efficient mass transfer mechanism that can improve contaminant removal while reducing the aggressive movement of liquor in the cleaning bath which may cause the entanglement of wool fibres.

A small amount of work has been published on implementing ultrasound in textile production. Work has included investigating the mass transfer effects and ultrasound transmission in an open width fabric scouring environment. Textile applications of ultrasound include open width fabric scouring, bast fibre separation, bleaching, removing weaving sizes, preparation for dyeing, nonwoven fabric consolidation, heat treatment and chemical coating. Only limited work has been published on wool cleaning with one paper investigating the improvements available to wool scouring by ultrasonic treatment at 25
kHz. Further work is required to assess the effect that ultrasound has on wool cleaning. Published ultrasound assisted wool dyeing research proposes that dyeing rate increases are due to ultrasound related energy and improved mass transport but do not consider ultrasound induced cuticle changes.

This study is devoted to identifying the advantages of using ultrasound in the cleaning of wool, and in doing so quantifies the effect that ultrasonic irradiation has on fibre surface morphology, fibre properties and dyeing rate. The thesis is divided into six chapters and these have been expanded on below.

Chapter one contains a critical review of literature focusing on the areas of: contaminants and cleaning mechanisms, wool fibre and its structure, wool cleaning, the theory of ultrasonics and ultrasonic cleaning, ultrasonic applications in textile fibres and ultrasonic dyeing. The Chapter covers problems, gaps and opportunities from the literature, preliminary studies, key hypotheses and an outline of the thesis.

Chapter two evaluates the effectiveness of ultrasonic irradiation during raw wool scouring. It is investigated in four parts with the first using residual grease content, scouring fibre loss, colour, entanglement and surface morphology to determine the optimum detergent concentration and temperature for scouring. The second part utilises mean fibre length after carding and mean fibre diameter after carding to evaluate the level of entanglement in ultrasound assisted scouring when compared with rake scouring. The third part utilises foil erosion to quantify ultrasonic cavitation levels within the wool scouring bath with reference to fibre loading. The fourth
part uses residual grease content, ash content and fibre colour to evaluate cleaning efficiency with reference to fibre loading.

Chapter three investigates the influence that ultrasonic irradiation has on domestic laundering. The work is investigated in four parts with the first part utilising fabric area shrinkage, thickness, colour and strength to evaluate the effect that repeated ultrasonic irradiated wash, dry cycles have on fabric properties when compared to hand washing. The second part utilises colour measurement to quantify the stain removal ability of ultrasonic irradiation, with an alkaline and acidic detergent, on the five common stains of coffee, tea, red wine, oil and an orange carbonated sugar drink. The third part investigates the effect that ultrasonic irradiation has on fabric weight loss and pilling during Martindale abrasion. The fourth part utilises an ICI pill box to determine if ultrasonic irradiation during laundering has an effect on pilling propensity.

Chapter four investigates the effect of ultrasonic irradiation on fibre surface morphology, tenacity and resistance to bending abrasion. The work was undertaken in three parts with the first part utilising scanning electron microscopy to determine the changes in fibre surface morphology after irradiation in a variety of cleaning liquor combinations. The second part employs single fibre bending abrasion resistance testing to determine if ultrasound induced changes to the fibre cuticle have had an effect on the fibre bending abrasion properties. The third part determines if ultrasound induced fibre cuticle changes have had an effect on single fibre tensile properties.

Chapter five quantifies the influence that ultrasound induced fibre cuticle changes have on wool dyeing rates. The work was undertaken in three parts
with the first part utilising fabric colour measurement during isothermal dyeing to evaluate the effect that pre-treatment with ultrasound has on dyeing rate. The second part utilises fabric colour measurement and dye-bath exhaustion during isothermal dyeing to determine the effect that treatment liquor composition has on dyeing rate. The third part utilises dye-bath exhaustion during isothermal dyeing to determine the level that ultrasonic induced fibre cuticle changes have on increased dyeing rates for ultrasound assisted dyeing.

The final Chapter summarises the main results achieved in this work and proposes the potential for future work.
1 Literature Review

1.1 Cleaning
Cleaning of a product is undertaken to remove the accumulation of surface contaminants that have resulted from nature, manufacture, or from use. There are five main mechanisms of cleaning and these are dissolution by a solvent, mechanical detachment, evaporation, chemical degradation and stain repellence. Cleaning can occur in a number of different ways at a number of different stages within textile processing and consumer use.

1.1.1 Contaminants
The nature of surface contaminants is varied. In textiles, the soil can be as simple as dirt picked up on wool from the animal laying on the ground in a field and as complicated as blood splatter in a surgical gown. Contaminants in textile garments are generally caused by the environment the item is used in, the fabric use and the practices and customs of the individual. With such a diverse range of contaminants it would be almost impossible to list all of the soil types. Getchell simplified the definition of a soil by explaining it as being made up of two general categories – a fluid component, usually an oil or a grease; and a solid component made up of small, more or less inert particles (Getchell 1955). Most contaminants are a mixture of the two components combined together.
1.1.1.1 The fluid component

There are many fluids that a textile fibre can come into contact with. As this work is based on wool cleaning, this part of the thesis will look at fibre contaminants in raw wool, contaminants picked up during processing and common fluid stains a wool fabric may be subjected to in use.

The fluid component of a contaminant by itself can provide a significant downgrading of a textile fibre. In raw wool, the most common fluid stains found are those excreted by the animal and these include lanolin, sweat (suint), urine and blood. They may also include oils and grease from the shearing process. Lanolin is commonly made up of two fractions – an oxidised fraction that is mainly found at the fibre tip and an un-oxidised fraction that is found at the fibre base (Dominguez et al. 2003). The oxidised wool grease is far harder to remove than the un-oxidised and forms complexes with other contaminants on the wool fibre or within a wool scouring bath.

Even though the presence of lanolin by itself on the surface of a wool fibre presents a contaminant problem, it can often contribute to further staining as it attracts, adsorbs and sticks particulate matter to the fibre surface. This phenomenon is not just limited to raw wool as oil based spinning lubricants are well known as a binding agent for dirt particles that have to be removed before dyeing or fabric finishing. Oil based stains can impact a fabric during a variety of fabric end use situations including; food preparation and consumption, human or animal secretion, skin and hair products, industrial processes and mechanical equipment.
The liquid component has been quantified for a number of different materials including raw wool (17.4±7.5% lanolin for 19.6±0.4 µm and 12.6±4.7% for 16.4±0.3 µm wool where the percentage is based on the weight of wool (Westmoreland et al. 2006)) and for textile garments (0.25% for shirts to 1.2% for collars based on the weight of fabric (Brown 1947)). The time of exposure to fluid based contaminants greatly affects their ability to be removed. Some fluids form a dry solid film in a short period of time whereas others take much longer, sometimes up to weeks and months after the initial exposure. Unsaturated oils and polymerisable substances and the solids that are bound by them become progressively harder to remove as they age after exposure (Getchell 1955).

1.1.1.2 The solid component
The solid contaminants present on a textile fibre can be as complex as the fluid components. They can be made up of both organic and inorganic materials derived from animal, vegetable and mineral origins. There are two main types of solid contaminant defined by the method of staining; general contamination and spotting. General contamination is the adsorption by the fibre or textile of contaminants such as dirt or dust that form a consistent layer on the fibre. General contamination could include the dust picked up by a wool fleece while the animal is in the field. It could also include dust forming on a table cloth over a period of time or a build up of sweat trapped dust on the collar of a tradesman’s work shirt. General contaminants tend to be microscopic particles that are generally air or surface borne. Spotting tends to be point contamination of the textile or fibre by a single compound like ink, food droplet, grass smudge or mud splatter.
Although general contamination over time can change the aesthetics of a textile, it is the spotting of individual stains that pose the highest degree of difficulty in cleaning. A single stain spot is made up of a large amount of the stain particles. Attempts at removal of the stain can result in only partial removal and this normally leaves the item with an intensity reduced visible spot. It tends to be the solid particles within a stain that make it visible and render the textile damaged. Particle size is an important factor in cleaning. Fine particles are more difficult to remove from a cleaning environment due to electrostatic attraction and their proximity to the surface. When an aqueous environment is used to remove fine particles they often sit within the liquid boundary layer close to the fibre surface and are unaffected by the moving cleaning liquor which is responsible for large particle detachment.

1.1.1.3 Contaminant retention
There are three main ways of retention of a contaminant onto a surface: chemical bonding with the fibre (including covalent and van der Waals), electrostatic attraction to the fibre and mechanical entrapment on the surface of the fibre or within the yarn or fabric structure (Schwartz 1949). Mechanical entrapment is one of the largest factors involved with sub microscopic, microscopic and macroscopic particle contaminants on a textile surface. Entrapment can occur within the fabric or yarn structure for larger particles and can also exist on surface imperfections or micro roughness for fine particles. The textured nature of the cuticle scale structure of wool fibres is perfectly designed for the retention of fine organic and mineral particles with accumulation occurring a the cuticle edge.
Chemical bonding in the form of direct contaminant to surface bonding depends on the nature of the contaminant and the reactivity of the surface. Relatively inert surfaces such as polypropylene provide few chemical bonding sites for contaminants. Liquids are more likely to become chemically bonded with a fibre as most fibre bonding sites are located within the structure of the fibre. The presence of a liquid bonded to a surface generally provides a point of mechanical entrapment or chemical bonding for a particle based contaminant. Some internal staining or contamination of a fibre can occur where the particle is small enough and generally dispersed within a liquid. This form of staining can be either through chemical bonding and/or mechanical entrapment of the stain and is commonly seen with dyes, metal complexes or inks. With wool, the presence of polar liquid can cause fibre swelling which in turn increases the gap between the cuticle scales allowing penetration of liquids and fine solids into the fibre structure.

Electrostatic charge of a textile surface can cause an increase in the number of particles that are attracted and bound to that surface. Electrostatic charge of a surface varies with a range of environmental factors including atmospheric conditions, particle movement near the surface and mechanical action on the surface. Electrostatic charge may provide an increase in initial attraction and bonding of a particle to a surface however long term surface particle retention is generally because of liquid bonding or mechanical entrapment.

1.1.2 Methods of Cleaning
Cleaning can be carried out in many ways with four mechanisms that can be employed to clean a contaminated article: firstly contaminants may be
dissolved by a solvent, secondly contaminants can be mechanically detached, thirdly contaminants can be evaporated and fourthly contaminants can be chemically degraded. A fifth mechanism is often proposed: the contaminant is repelled by a stain repellent surface. However, this is avoiding a stain rather than cleaning. A diagrammatic depiction of the four cleaning mechanisms is given in Figure 1.1. Most cleaning methods employ a combination of these mechanisms for contaminant removal.

**Figure 1.1** Four cleaning mechanisms

1.1.2.1 **Solvent cleaning**
Most cleaning systems involve the use of a solvent to help dissolve or detach contaminants from the surface being cleaned. There are two main types of solvent cleaning. The first type is the use of a solvent to dissolve contaminants or the fluid component that binds them. The second type uses the solvent as a carrier for chemicals that dissolve, or degrade contaminants or the fluid
component that binds them. Both systems may use mechanical agitation of the solvent and/or item being cleaned to mechanically detach contaminants. Movement of the solvent is used to provide fresh cleaning chemistry at the surface of the contaminant, otherwise movement of the cleaning chemistry to the surface and removal of the stain are done by diffusion which is rate limiting.

1.1.2.1.1 Dry cleaning

In textile dry cleaning the item to be cleaned is agitated in an organic solvent that dissolves contaminants or the fluid components binding the contaminants. The agitation helps to transfer the solvent through the fabric and dislodge loosely bound particles. The dissolved contaminants, solvent and dislodged particles are drained off from the cleaned item after the batch washing process. The most commonly used solvent is tetrachloroethylene or as it is commonly known in the textile dry cleaning industry “perchloroethylene” (PERC) (Orban 2004). PERC is not without its environmental problems, however most of these have been minimised by the development of dry cleaning equipment (Orban 2005).

Solvents such as trichloroethane are used to spot out point contamination (Orban 2004). In spotting contaminants are dissolved or displaced by the solvent as it contacts with them. The force of the solvent being propelled through the contaminated fabric helps to dislodge undisolved stains and these are absorbed by a blotting fabric and carried away from the cleaned item. Excess solvent evaporates from the fabric after the spotting process is completed.
1.1.2.1.2 Aqueous cleaning

Most domestic and commercial textile cleaning processes are conducted using a water based cleaning liquor. Water alone is not an effective solvent for removing contaminants from the surface of fibres. Other agents need to be added to the solvent to help in detaching and emulsifying contaminants. These agents can include detergents and sequesterants. In some applications the stain is also degraded by using either an oxidative or reductive bleaching agent. The process of aqueous scouring is similar to that involved in dry cleaning. The item to be cleaned has a transfer of the liquor through it, enabled by the cleaning equipment. The liquor transfer can be produced by high pressure jets, sprays and squeeze points. Alternatively the item to be cleaned may be agitated within the liquor or dunked and withdrawn from the liquor to promote liquor transfer.

Aqueous cleaning can take place at many stages during the processing of textiles. Fibres such as wool can be scoured before yarn processing, fibre, yarn and fabric can be washed before the dyeing process, fabric can be washed before or during the finishing process and garments can be washed during or after their manufacture. The end of manufacture is not the end of the washing process. Most garments will be laundered many times before the end of their life cycle. At present all of these processes for laundering during or after manufacture are variations of the aqueous and dry cleaning process as given above.
1.1.2.1.3 Detergents

A detergent helps to remove a stain from the surface of an item by attaching to the substrate and contaminant surface. The micelle structure of the detergent attaches to the surface of the substrate and the contaminant and increases surface wetting. The contact angle ($\theta$) between the stain and the surface increases and this reduces the energy of adhesion (Figure 1.2). The contaminant is now easier to remove by liquid movement or mechanical detachment.

For a hard flat surface Young’s equation (Young 1805) best represents the contact angle of the contaminant on the surface (Equation 1.1).

\[
\cos \theta = \frac{\gamma_{sl} - \gamma_{sc}}{\gamma_{cl}}
\]  

(1.1)

Where $\gamma_{sl}$ is the surface tension of the substrate/liquid interface in mN/m, $\gamma_{sc}$ is the surface tension of the substrate/contaminant interface in mN/m and $\gamma_{cl}$ is the surface tension of the contaminant/liquid interface in mN/m.
Once removed from the surface the contaminant is surrounded by the detergent micelles which help to avoid re-deposition of the particle onto the cleaned surface.

1.1.2.1.4 Detergent formulations

Cleaning is carried out using a blend of chemicals that are designed to combat different types of soiling. Apart from the surfactant, chemicals to perform sequestering, bleaching, pH control, corrosion inhibition, perfumes, dyes, foam regulators, anti re-deposition agents, enzymes, optical brighteners, fillers, bleach activators and bleach stabilizers can be found in most commercial detergent mixes (Lange 1994). Each soil type and application requires a special formulation to target the stains present.

Bleaching is commonly carried out on some stains to reduce the colour of soil staining and to improve the whiteness of the substrate (Jakobi and Lohr 1987). Most bleaches used in detergents are oxidants. The most common chemical used is sodium perborate monohydrate (NaBO₃.H₂O) followed by sodium percarbonate (Na₂CO₃.1.5H₂O₂). Wool does not stand up well to bleaching during laundering however most proprietary products still contain a moderate level of bleach to help improve their cleaning performance. Most utilize an optical brightening agent as well as the bleach.

Complexing agents are employed in a detergent mix to remove the effects of water hardness. Water hardness can cause the precipitation of the inorganic salts and the surfactant. The use of a complexing agent leads to the creation of a soluble complex that will not precipitate out onto the surface of the fabric being washed. Among the complexing agents, sodium tripolyphosphate
(STTP) holds a dominant position (Falbe 1986). Due to polluting effect of phosphate on freshwater ecosystems it has been reducing its market dominance to be replaced by environmentally friendly products such as Zeolite A. Ethylene diamine tetraacetic acid (EDTA) is also an important complexing agent for the removal of heavy metal ions.

1.1.2.2 Physical detachment
If a particle is loosely bound to a surface it can generally be removed by physical detachment. Physical detachment is normally only able to be achieved on contaminant particles or large droplets of liquid. To detach a contaminant particle the surface or the particle is hit by a sudden force that causes a breaking of the bonds binding the particle to the surface. The most common form of physical detachment is where the particle is impacted on by a jet of liquid or gas that dislodges the particle. In aqueous cleaning the particle would need to protrude out of the boundary layer of the surface so that it can be impacted on by the turbulent movement of liquor in the bath. Alternatively the surface can be impacted suddenly which causes the surface to accelerate away from the stationary particle causing detachment. Physical detachment is normally combined with solvent cleaning.

1.1.2.3 Evaporation
The cleaning of a surface can be achieved by the evaporation of the organic material bound to the surface. Cleaning by evaporation can only be achieved if the surface being cleaned has a higher temperature or pressure of evaporation than the contaminant. In order to clean by evaporation the surface is subjected to either heat, low pressure or a combination of the two. The contaminant burns off into a gaseous state and is removed from the surface.
An interesting application of this is the self cleaning oven. In a self cleaning oven the heat of the oven gets to a point (>500°C) where contaminants on the surface of oven start to evaporate or thermally degrade into particles that will evaporate or no longer stick to the oven surfaces. This style of cleaning is limited in its application as the item must be able to withstand high temperatures. This method of cleaning is adopted with some fibre ceramic filter material where the filter is sintered to burn off any contaminants in order to refresh the filter.

1.1.2.4 Chemical degradation
Chemical degradation can occur due to the chemical nature of the surface that is contaminated or by a chemical agent exposed to the contaminant on the surface. Both of these systems have seen use in textile products. The most common form of chemical degradation in textiles is the bleaching of stains on the surface or within the structure of a textile fibre. The common bleaching agents used are oxidative in nature and include hydrogen peroxide (H₂O₂), sodium hypochlorite (NaOCl), sodium chlorite (NaClO₂) sodium perborate (NaBO₃) and sodium percarbonate (Na₂CO₃·1.5H₂O₂). Reducing agents like sodium dithionite (Na₂S₂O₄) and sodium thiosulphate (Na₂S₂O₃) can also be used. A bleaching agent is used to break organic bonds which discolour the contaminant or break its bond with the contaminated surface.

The other form of chemical degradation of an organic contaminant on a surface is by a photo-catalytically active metal oxide surface. The metal oxides with this function can include titanium dioxide (TiO₂), tungsten oxide (WO₃), and zinc oxide (ZnO). The surface is said to be self-cleaning, which is not strictly true as the surface must be exposed to light at the correct wavelength for the
process to work. With TiO$_2$ ultra violet (UV) irradiation of a photon of energy greater than or equal to TiO$_2$ band gap energy (hv>3.2 eV, i.e.$\lambda<380$nm), electron-hole pairs are formed. The free electrons and electron holes interact with organic matter present at a TiO$_2$ particle surface initiating chemical reactions. Through a complex set of heterogeneous chemical reactions an oxidative decomposition of an organic molecule can take place. The organic molecules are broken down into species such as water (H$_2$O), carbon dioxide (CO$_2$) and nitrogen dioxide (NO$_2$).

Thin coatings of a metal oxide on a surface of a substrate can be said to have a self cleaning effect. Several researchers have reported their effects on degrading organic compounds (Daoud and Xin 2004; Qi et al. 2006; Hurren et al. 2008). Most contaminants are organic based or bound to the surface by an organic molecule. These organic molecules are catalytically degraded and as the species after catalysis are colourless they no longer are considered a stain and hence pose no problems.

### 1.2 Wool Fibre Structure

#### 1.2.1 Fibre Structure

The wool fibre has a complex structure which it shares with other keratin fibres like alpaca, mohair, cashmere and human hair. The simplified fibre consists of inner cortical cells surrounded by one or more layers of cuticle cells (Maclaren and Milligan 1981; Hocker 2002). Figure 1.3 shows a cross-section of a 20 µm wool fibre with each element defined. The cortex is responsible for 90% of the fibre mass and consists predominantly of two different types of cortical cells,
ortho (60 – 90%) and para (40 – 10%) (Hocker 2002). The cuticle is responsible for the remainder of the fibre mass and is made up of three layers; endocuticle, exocuticle and epicuticle.

Figure 1.3 20 µm Merino wool fibre structure (Hocker 2002)
1.2.2 Fibre Cortex
The fibre cortex is composed of spindle like cells that have a length between 45-95 µm and a width of 2-6 µm. The cortical cells are made up of 5-20 macrofibrils bound together in a matrix of cytoplasmatic and nuclear remnants of the keratinocytes. The macrofibrils are made up of bundles of 500 to 800 microfibrils (Hocker 2002). The composite structure of the cortex is responsible for the bulk of the tensile strength of a wool fibre (Hearle 2002). The overlapping nature and poor bonding between the cuticle structure provides limited resistance to tensile strain.

1.2.3 Fibre Cuticle
The cuticle of a wool fibre is made up of a number of nearly rectangular cell sheets, often referred to as scales due to their resemblance to fish scales. The cuticle cells surround the outer edge of the fibre cortex and overlap the next cell (Figure 1.4). The cuticle is considered to be made up of three distinct layers starting from the outside with the epicuticle, exocuticle and endocuticle (Figure 1.5). The epicuticle is drawn below with a separate F layer to highlight this surface. The epicuticle is actually highly acylated with fatty acids of 18-methyleicosanoic acid which makes the cuticle surface highly hydrophobic and provides the fibre with its resistance to quick wetting, and attack from alkalis, oxidising agents and proteolytic enzymes. The fatty acid structure is about 2.5 nm thick and amounts to approximately 0.1% of fibre weight (Negri et al. 1993; Hocker 2002). The intricacy of the scale structure and its hydrophobic surface is the limiting factor to penetration of dye molecules into the fibre as they must pass between the scale structure in the space between the cuticle cell overlap (Lewis 1992).
Australian Wool Innovation commissioned Canesis Network Limited to undertake extensive work on measuring the cuticle structure of 20 µm diameter Merino wool fibres. Utilising modern scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques enabled them to provide detailed information on a large number of wool fibres that either agreed with or superseded work by a number of researchers in this field (Makinson 1979; Maclaren and Milligan 1981; Kong et al. 1989; Lewis 1992; Hocker 2002). The work found that most fibres were surrounded on average by four cuticle cells around the fibre circumference (range 3-8). The cells were approximately 27 µm long and 28 µm wide and 360 nm thick. The layering of the cells was different depending on the adjacent cortical cells with two to three cells thick adjacent to the paracortex and one cell adjacent the orthocortex. The average thickness of the entire cuticle cell wall was 670 nm
but again the cells adjacent to the orthocortex were 600 nm and the paracortex 750 nm. The mean height of the cuticle scale edge was 0.83 µm and had an edge angle of 97º (Walls et al. 2006).

1.2.4 Fibre Damage, Felting and Appearance Change

1.2.4.1 Fibre damage
Fibre damage can occur to a wool fibre in washing by a range of different factors. The most common of these are temperature and alkali degradation of the fibre. Mechanical damage to the fibre by movement within an aqueous system may also occur.

Fibre damage by alkali occurs when the alkali attacks the disulfide bonds within the wool structure. The disulfide bonds are responsible for crosslinking of the fibre structure and contribute to the strength of the fibre. Cystine breakdown in the presence of alkali results in fibre yellowing (Norton and Nicholls 1964). Significant exposure to strong alkali solutions in a warm environment can dissolve the wool fibre. Exposure to high temperature for long periods of time can yellow the wool fibre and reduce its strength. Yellowing is caused by the interaction between amino and carboxyl groups (Norton and Nicholls 1964).

Mechanical agitation can affect the fibre. Abrasion of the fibre can occur where the fibre is abraded by a moving part of the cleaning equipment. Fibre abrasion can lead to surface damage, fibre deformation and even fibre breakage (Liu et al. 2005). The first step of fibre abrasion is the removal of the scale structure of the fibre exposing the cortex fibrils.
1.2.4.2 Felting
Irreversible entanglement of wool fibre, better known as felting, is the largest factor impacting the quality, ease of processing and appearance of a wool product after it has been washed (Blankenburg 1969). Wool felting during scouring reduces processing yields and mean length of processed fibres due to increased fibre breakage (Christoe 1986; Bateup and Christoe 1996). The mechanism of fibre felting is very complicated and research findings reported in the literature are not always consistent. Felting is a form of tangling produced by the persistent migration of individual fibres in the tip-to-root direction, which is caused by the directional frictional effect of fibres (DFE) (Mercer and Makinson 1947; Makinson 1964; Makinson 1979). DFE is important when considering the felting of animal fibres because their frictional characteristics are anisotropic. The friction to move the fibre in the tip to root direction is greater than in the root to tip direction. This difference in directional friction is caused by topographical asymmetry. Fibre surface topography is different for different fibres. An example is alpaca fibre that has a smaller scale height and a larger scale frequency per unit of length than wool (Liu et al. 2005). Interlocking of the scale structure causes fibre migration to be an irreversible process. Fibre migration is increased significantly when the wool is placed in a warm, moist, lubricated environment in the presence of mechanical agitation (1997). These conditions are found in most wool cleaning systems, with the detergent acting as the lubricant.

The effect that felting has on a wool product depends on the point at which the felting occurs. Felting makes fibres hard to separate for further processing such as carding and top-making. Felting during wool scouring results in reduced top
making efficiency (Christoe 1986). Entangled fibres are easily broken during carding, gilling and combing which causes a decrease in mean fibre length (eg. Hauteur and Barbe). Felting in fabric can have many effects depending on the level of fibre movement. Very low levels of felting provide fibre movement and relaxation within the yarn structure of the fabric. This is called “burst” in fabric finishing and can result in a softening of the fabric and an improvement of drape (Brady 1997). As felting increases, the weave or knit structure is slowly obscured. The fibres move out of the yarn structure and become randomly orientated within the fabric. Higher levels of felting are accompanied by a dimensional shrinkage of the fabric. Within a manufacturing environment the dimensional shrinkage poses no problem where the product is being felted as part of the manufacturing cycle and shrinkage is engineered into the initial fabric width. Undesired felting during processing or during garment laundering can cause damage or destruction of a wool product and should be avoided.

Felting caused by the movement of fibre in a moist or wet environment is significantly higher than movement in a dry environment due to the fibre swelling caused by exposure to water. During aqueous cleaning movement is caused by the method of liquor transfer through the item being cleaned. The more agitation provided to the fibres then the higher the level of felting observed. The level of contaminant removal is directly proportional to liquor movement at the surface of the fibre so selection of the method of liquor movement must minimise fibre movement but maximise liquor to fibre interaction.
1.3 Wool Cleaning

Wool requires cleaning in at least two points along its processing path and many times during its product lifetime. The main points wool is cleaned during manufacture are during raw wool scouring, before dyeing, before fabric finishing and after garment manufacture. Raw wool is scoured before processing to remove grease and dirt. Fibre, yarn or fabric is washed before dyeing to remove contaminants, spinning lubricants and weaving sizes that could interfere with the dyeing process. Fabrics are washed before fabric finishing removing contaminants obtained from the mill or previous processes that could interfere with the finishing process. Garments are washed to remove processing oils and contaminants picked up during their manufacture and to provide a bulkier and softer handle.

The washing of wool poses many technical problems. Wool has scales on its surface that cause fibre entanglement (felting) during agitation in a moist environment. Washing systems need to be designed to minimise fibre movement but maximise liquor transfer so as to avoid felting but still achieve a high level of cleaning. Wool suffers from strength loss and degradation in highly alkaline environments. Most natural soaps are alkaline so synthetic detergents need to be selected to work within the slightly alkaline (pH 8.5) to acidic pH range.

1.3.1 Raw Wool Scouring

Raw wool scouring is done to remove contaminants from the fibre that would otherwise impede further processing of the wool fibre or affect the handle and look of the finished product. Contaminants removed during scouring can be
divided into four main groups: wool wax, suint, dirt and proteinaceous matter (Halliday 2002). A fifth contaminant, vegetable matter is also commonly found in wool however this is not significantly removed during the scouring process. Wool wax or grease is essentially a fatty matter secreted from the sebaceous gland of the sheep and is predominantly lanolin. Suint is a water soluble material consisting essentially of organic and mineral potassium salts and is from the sheep’s sweat or sudoriferous gland. Dirt is an inorganic material such as earth that is picked up from the environment where the sheep was living and may include faeces excreted by the animal. Proteinaceous matter is organic matter from the sheep’s body and can include dislodged wool scales and skin (Elling and Zhan 1989). All of these contaminants are present in a wide variety of concentrations and are influenced by things including the sheep’s age, breed, health and living environment (Westmoreland et al. 2006).

Although many systems for scouring have been developed only two systems have gained any wide use. These two systems are hot aqueous detergent scouring and solvent scouring. Both systems have their advantages and disadvantages. In aqueous scouring, detergent, water, temperature and mechanical movement of the scouring liquor act to remove the contaminants from the wool. Aqueous scouring is usually carried out under conditions of moderate temperature (50°C plus) and high detergent concentration, hence it involves high consumptions of water and energy and produces large volumes of high chemical and biological oxygen demand effluent (Halliday 2002). Fibre entanglement is a major problem as the agitation of the rakes in a warm, moist alkaline environment promotes fibre felting, which leads to increased fibre breakage in top-making (Christoe 1986). Inconsistent control of variables
including temperature and alkali concentration can lead to significant damage to fibre properties including colour and strength (Christoe 1986). With solvent scouring the equipment utilised is complex and requires careful monitoring to maintain safe operation and avoid release of solvent to the environment. Most solvents pose a moderate to high risk to the operators and the environment. A large amount of dust remains in the fibre after scouring and this causes increased wear on downstream processing equipment. These factors have combined to reduce the adoption of solvent scouring (Westmoreland 1998; Halliday 2002).

1.3.1.1 Aqueous scouring
In aqueous detergent scouring emulsification of the grease on the fibre surface is the most important process. The wool fibre is first opened to facilitate liquor movement through the fibre. The fibre is then conveyed to a series of baths of warm alkaline liquors containing either soap or detergent. The wool is submerged in the liquor periodically as it passes through the bath by means of a reciprocating rake, harrow or dunking roller. The rake also facilitates propulsion of the fibre from the entry to the exit point of the bath. During this time, the exposure of the grease to the detergent in the hot alkaline liquor causes a dissolving and emulsification of the wool grease. Suint is also dissolved by the water present in the solution. The mechanical action of the rake causes most of the dirt particles and proteinaceous matter to be detached from the fibre. This settles to the base of the bath where it is carried out with the flow of the outgoing effluent. Between each bath there is a high pressure squeeze roller where further dirt and grease is carried off with the expelled
liquor. After the baths the fibre is hot air dried to evaporate off any scouring solution not expelled by the final squeeze roller.

Aqueous scouring systems currently in use include the WRONZ mini-bowl system (Smith 1989), SIROSCOUR system (Christoe and Bateup 1995) and the Fleissner Drum scour (Westmoreland 1998). Most aqueous scouring lines have five to seven baths (Westmoreland 1998; Halliday 2002). The first three baths generally have detergent and alkali added to them whereas the last baths contain only heated water. The latter baths are used for rinsing and removal of residual detergent whereas the initial baths are used for contaminant removal. Some scouring lines can also have a cold suint bath at the start of the scouring line that contains only cold water. This bath is used to remove a portion of the suint and dirt before the alkaline detergent baths.

1.3.1.2 Solvent scouring
In solvent scouring, the solvent dissolves the wool grease efficiently, however it is generally ineffective in the removal of wool suint, dirt, and proteinaceous matter (Halliday 2002). The processing path for solvent scouring requires the wool to be placed into a sealed chamber. The fibre is then exposed to a solvent that dissolves the grease and other solvent soluble contaminants. The solvent is then extracted from the fibre and the fibre is processed through equipment to remove some of the residual dust, dirt and proteinaceous matter. Some processes use small amounts of water added into the solvent stage to remove suint. The technology has not been widely accepted with very few solvent scouring plants currently running (Halliday 2002).
1.3.1.3 Fibre parameters measured after scouring
The scouring of wool fibres is undertaken to remove dirt, grease and suint. The main measurements undertaken on raw and scoured wool are grease content/residual grease content, ash content, colour, vegetable matter, moisture content, scouring yield, fibre strength, fibre diameter and fibre length. Fibre length after carding may be measured to determine fibre entanglement from the scouring process. Vegetable matter and moisture content are not variables affected by scouring so they will not be discussed further.

1.3.1.3.1 Grease content
Residual grease content of a scoured fibre is important. If the level is too high from inefficient scouring it can result in poor processing performance especially with fibre build up on rollers (Christoe 1986). The traditional method for determining grease content within a wool fibre sample is to undertake a multiple stage solvent extraction process in Soxhlet extraction glassware using solvents such as dichloromethane or ethanol. This is a slow process requiring accurate sample preparation and weighing followed by 4 – 6 hrs within the soxhlet device. Recent developments have shown that Near Infra Red (NIR) spectroscopic analysis can be used to predict wool grease levels in wool fibre (Baxter 2002). This method must first be calibrated with a number of Soxhlet extraction tests in tandem with the NIR measurements but has been adopted into the standard test method by the International Wool Textile Organisation (IWTO). NIR is preferred due to the shortness of time for measurement and it can be used to evaluate a number of different fibre parameters in one measurement. The main test methods are IWTO-10-03 (International Wool Textile Organisation 2003a) for Soxhlet residual grease
content and IWTO DTM-43-98 (International Wool Textile Organisation 1998a) for NIR measurement.

1.3.1.3.2 Ash content
Ash content testing is conducted to determine dirt and inorganic matter content of wool fibre. An excess of dirt within a fibre caused by inefficient scouring results in excessive wear of equipment and an increase in cleaning stoppages during processing (Christoe 1986). Ash content is measured by burning at high temperature a known mass of wool fibre and then measuring the weight of the remaining ash. All organic matter should be burnt off leaving only the inorganic matter behind. The test is slow and the process produces flue gases that are both harmful to the environment and a smell problem to the area surrounding the test facility. Recent developments have seen replacement of the ash content test with a NIR approximation of ash content similar to that seen for grease content. Both variables can be estimated with the one NIR measurement (Baxter 2002).

1.3.1.3.3 Colour
Colour is measured after scouring using a spectrophotometer. Colour is an important factor to measure as it is affected by inefficient scouring and/or too much alkali and too high a temperature during scouring. It affects the appearance of end products and poor colour can significantly devalue the fibre. New technology is currently being developed to incorporate colour measurement with NIR measurement of grease and ash content (Baxter 2002). The main test method for colour evaluation is IWTO-35-03 (International
Wool Textile Organisation 2003c). Colour is normally expressed using either a yellowness or whiteness index.

1.3.1.3.4 Scouring yield

Scouring yield is calculated using the mass of a greasy wool sample and the mass of the same sample after laboratory scouring. Scouring yield is the mass of useable wool after scouring and is determined for the purpose of companies to be able to estimate the value of a wool fleece. The main test method is IWTO-19-03 (International wool Textile Organisation 2003b).

1.3.1.3.5 Fibre strength

Fibre strength is measured commercially as bundle breaking strength in the greasy staple. The main test method is IWTO-30-07 (International Wool Textile Organisation 2007). It is measured to allow a manufacturer to avoid purchasing tender wool weakened due to growing conditions and is not relevant to wool scouring.

Strength measurement of a fibre after scouring is important in predicting the performance of the scouring process but is rarely undertaken due to the time required per measurement and the number of measurements required for statistical accuracy. Strength is significantly affected by pH and temperature of the scouring bath. Single fibre strength measurement for wool fibres can be conducted using a variety of different constant rate of extension machines fitted with an accurate load cell. For accurate measurement of single fibre strength it is important to conduct diameter measurement along the full length of the fibre to be broken before undertaking strength measurement. BSC Electronics (Perth, Australia) have developed two single fibre diameter and
tensile machines that achieve both measurements in the one machine and these are called a single fibre analyser or SIFAN.

1.3.1.3.6 Fibre diameter

Fibre diameter and fibre curvature is an important measurement after scouring as curvature can be affected by temperature in the scouring process. Diameter can also be affected by temperature and fibre entanglement but this is generally not observed until after carding and top-making and hence is discussed further in length after carding. Diameter measurement is normally conducted using either IWTO-6-98 (International wool Textile Organisation 1998b) with an airflow device, IWTO-47-09 (International wool Textile Organisation 2009b) with an Optical Fibre Diameter Analyser (OFDA) or IWTO-12-09 (International wool Textile Organisation 2009a) with a Laserscan device.

1.3.1.3.7 Fibre length

Fibre length is not normally conducted accurately in a greasy state or after scouring however it is commonly measured after carding and top-making due to the design of the automated measurement equipment. Fibre length is important because excessive entanglement, temperature or pH degradation can result in excessive fibre breakage during carding and top-making which reduces the mean fibre length. The main test methods for determining fibre length are IWTO-17-04 (International Wool Textile Organisation 2004) using an Almeter, IWTO DTM-16-02 (International wool Textile Organisation 2002b) using a WIRA fibre diagram, IWTO DTM-1-02 (International wool Textile Organisation 2002a) using a comb sorter and a newly developed process using an OFDA4000 (Brims 2002).
1.3.1.3.8 Fibre length after carding

Fibre length after carding is an important parameter for determining the level of entanglement or temperature/pH damage occurring from scouring. The fibre is first processed through a sample carding machine before being measured for length using one of the methods mentioned in Section 1.3.1.3.7. The standard test method is NZS8719 (Standards New Zealand 1992). Diameter can also be measured at this point to determine diameter change before and after carding and both measurements can be achieved simultaneously if the OFDA4000 is used for length measurement.

1.3.2 Preparation and Finishing
1.3.2.1 Washing before dyeing
The process of washing wool fibre, yarn or fabric before dyeing is an important step in the textile colouration process. It is important to have a thorough and consistent removal of contaminants otherwise unlevel dyeing may occur. Dyeing can occur in a range of different forms including loose fibre, top, yarn in package or hank form, fabric and garment. Cleaning is normally conducted in the dyeing machine with a combination of a surfactant and a pH control agent. Ultrasonic irradiation to improve contaminant removal could be conducted but would not be applicable to all processes due to the packing density of the item being dyed. Long liquor volume machines like fabric winch, fabric jet, fabric jig (Vouters et al. 2004), garment rotary drum and garment paddle dyeing machines could be easily adapted to incorporate ultrasound during the cleaning and dyeing steps.
1.3.2.2 Open width scouring and wet finishing
Open width scouring and wet finishing is conducted to remove contaminants, processing aids like spinning lubricant and to improve fabric handle. It is commonly performed on fabrics in a continuous washing range, before stentering and for very delicate fabrics that require some wet processing to provide burst. Fabric burst during wool wet finishing is conducted to change the fabric structure by movement in a wet environment. The process involves the removal of most spinning and weaving tensions from within the fabric and can go as far as migration of some fibres from within the yarn structures. The process utilises fibre and yarn movement brought on by the initial stages of felting. The result is a softer fabric that has better drape. Most worsted fabrics will be processed to have a small degree of burst before dry finishing. Scouring is achieved by passing the fabric through one or more baths containing detergent and a pH control chemical. In a continuous wash range the detergent step is followed by a series of rinses including spray rinses to remove the detergent and released contaminants. Open width machines may easily be modified to allow use of ultrasonic irradiation with an ultrasonic horn/plate combination (Gallego-Juarez et al. 2009).

1.3.2.3 Garment finishing
Garment finishing, like wet finishing, is conducted to remove contaminants from production including processing aids. Garment wet finishing is also conducted to provide bulk and softness in the fabric by removing some of the stresses placed into a yarn and fabric during manufacture. A detergent is commonly used with a pH control agent, however it can sometimes be conducted with just warm water. The process is generally conducted in either a machine with an overhead paddle system or in a perforated drum in a partially
filled bath. Both processes could be improved by ultrasonic irradiation during the cleaning step of the process.

1.3.2.4 Parameters measured
The main parameters assessed after cleaning during processing are colour, dimensional change, strength, appearance, drape, pilling and resistance to abrasion. Each of these is directly affected by the cleaning process and should be considered when evaluating the effects of ultrasonic irradiation during the process.

1.3.2.4.1 Colour
Colour is one of the most important factors to measure when accessing scouring efficiency and effectiveness. Most contaminants cause a discolouration to a fabric hence an improvement in colour is observed if the contaminant is effectively removed. Cleaning processes can still cause temperature and alkali yellowing of the fibre so colour measurement is also used to evaluate this factor. A spectrophotometer is normally used and colour is expressed in terms of yellowness or whiteness index for griège fabrics and CIE colour space or Delta E change for coloured fabrics (Hurren 2008).

1.3.2.4.2 Dimensional change
Whenever a fabric goes through a wet processing stage it can change dimensions. With fabrics other than wool and fabrics not constructed into a garment then this dimension change can be reversed during drying in a stenter. Wool fabric can undergo irreversible dimensional shrinkage during wet finishing. Wool fabrics should be measured for dimensional change before and after a cleaning step to ensure that agitation of the fabric during cleaning is not
causing excessive shrinkage. Dimensional change is measured by marking four points on a fabric on the points of a square shape at a known distance before cleaning. After cleaning and drying the distance change is measured and the percentage area change calculated. Dimensional change can also occur in the form of spirality where the residual torque in the yarn skews the angle of the warp and weft of the fabric after wet treatment. This is normally only caused by yarn production parameters.

1.3.2.4.3 Strength

If a fabric is damaged by the cleaning process then this damage is normally reflected in a change of tensile strength. Strength can be measured in two main ways: a direct tensile test or a burst strength test (Wang et al. 2008). Strength is changed by excessive temperature, pH, chemical attack or significant dimensional change from mechanical interference.

1.3.2.4.4 Appearance change, abrasion and pilling

Appearance change and pilling (described together as pilling) is normally measured either as a visual appearance change or in an automated measurement of surface topography change. Appearance change is normally caused by excessive mechanical agitation of the fabric during cleaning. It may be affected by chemical degradation, pH and temperature. Propensity for pilling is evaluated with either the ICI pill box or Atlas random tumbler followed by visual or automated assessment (Wang et al. 2008). Abrasion resistance is affected by the same parameters as pilling. Abrasion resistance is normally measured by Martindale abrasion where a known abradant is rubbed
in a non-repeating motion over the surface of the fabric for a predetermined number of cycles.

1.3.2.4.5 Drape

Drape of a wool fabric is changed initially by relieving the stresses of manufacture and then by felting. A relief of processing stresses is normally observed by an improvement in drape whereas felting tends to make the fabric stiffer and reduces its drape. Drape can be measured as either a change in bending angle or as draping over a circular hanger (Cuisak drape tester) (Wang et al. 2008). The measurement should be done before and after the cleaning step.

1.4 Ultrasonics

1.4.1 History of Ultrasonics
The first scientific evidence of ultrasonic energy was seen during the early tests of the first British destroyer in 1894. John I. Thornycroft and Sydney W. Barnaby (Thornycroft and Barnaby 1895) noticed that the high rotational speed of the ships propeller caused severe vibration. They suggested that the effect was caused by large bubbles or cavities formed by the spinning propeller imploding due to water pressure. They subsequently redesigned the propeller to reduce the vibrations caused by what came to be known as cavitation. As the Navy produced faster propulsion systems cavitation became an increasingly significant problem. The British Navy commissioned Lord Raleigh to study this phenomenon further and he confirmed that the vibrations were due to the
enormous turbulence, heat and pressure of the imploding cavities (Raleigh 1917).

At the same time experiments by Langevin undertaking research into the underwater detection of submarines were utilising quartz transducers at a resonance frequency of 50 kHz (Graff 1981). The researchers noted that fish were killed by the sound beam but undertook no further research in the matter. In 1924 Van Dyke noticed the searing of skin when a resonant quartz bar was touched but like Langevin took no steps to investigate these early observations fully (Graff 1981).

The first published experiments into ultrasonic irradiation were conducted by Alfred L Loomis and R. W. Wood in 1927. The experiments were conducted in Loomis’s garage using a General Electric vacuum-tube oscillator and a quartz plate transducer immersed in an oil filled dish (Wood and Loomis 1927). Their work examined a range of different effects including vibration of solids, heating of liquids and solids, effects on biological cells, effects on animals and chemical reaction. Publication of this work led to a range of different work that extends through to the current day.

1.4.2 Theory of Ultrasonics
The chemical effects of ultrasound can be summarised into three distinct areas: homogeneous sonochemistry of liquids, heterogeneous sonochemistry of liquid/liquid or liquid/solid systems and sonocatalysis (Suslick 1994). Each of these sonochemistry reactions are driven by the phenomenon of cavitation, hence liquids must be involved. Chemical reactions do not generally occur during the ultrasonic irradiation of solids or solid/gas systems. The wavelength
between successive compression waves of ultrasound is between 10000 µm to 100 µm depending on the frequency (Suslick 1994). These wavelengths are not comparable to molecular dimensions hence there are no chemical effects from direct interaction of ultrasound with molecular species.

1.4.2.1 Cavitation
Cavitation is the generation, growth and collapse of cavities resulting in very high energy densities of the order of 1 to 10<sup>18</sup> kW/m<sup>3</sup> (Gogate et al. 2006). The implosive collapse of a cavitation bubble can generate huge amounts of energy at the bubble collapse location in the form of heat (5000°C) and pressure (1000 atm) however the ambient conditions of the liquid remain relatively unchanged. Free radicals produced due to a disassociation of vapours within the cavitation bubble can intensify chemical reaction rates or produce unexpected reactions (Suslick 1989; Suslick 1990; Gogate et al. 2006). Cavitation generated turbulence along with micro-streaming during bubble oscillation help to enhance the rate of transport processes. High pressures and energy from bubble collapse can cause significant mechanical damage to metal surfaces or rupture dispersed solid particles.

There are four main ways to generate a cavitation collapse within a liquid and these are acoustic cavitation, hydrodynamic cavitation, optic cavitation and particle cavitation. Only acoustic and hydrodynamic cavitation have found their way into industrial processing with ultrasonics as optic and particle cavitation only provide single point cavitation within a liquid.
1.4.2.1.1 Acoustic cavitation

Acoustic cavitation is achieved by irradiating a liquid using a high frequency sound wave (16 kHz – 100 MHz) which causes pressure variations within a liquid. Ultrasonic irradiation produces a high number of cavitation events dispersed within the irradiated liquid. Acoustic cavitation is commonly used for irradiating a bulk liquid within a bath and is normally used for cleaning, chemical reactors and some solid fragmentation. Cavitation in a bulk liquid by acoustic irradiation results in two common forms of cavitation and these are cavity collapse in a homogeneous liquid and cavitation near a liquid/solid interface.

1.4.2.1.2 Hydrodynamic cavitation

Cavitation is produced by pressure variations caused by a liquid converting from a very high pressure to a low pressure. Cavitation occurs in a single step where the cavitation bubble forms, grows to an unstable size and implodes. This is normally achieved by a system utilising velocity variations to produce the difference in pressure. These devices include high speed impellors, orifices and venturi. Due to the relative size of the devices this cavitation is restricted to dispersion, homogenisation, chemical reactions and particle fracture.

1.4.2.1.3 Optic cavitation

Optic cavitation occurs when photons of high intensity light are radiated onto a fixed point within a liquid rupturing the liquid continuum. Lasers are the best source of photons, however this technology is limited in industrial application due to the small number of cavitation events.
1.4.2.1.4 Particle cavitation

Particle cavitation is similar to optic cavitation however the liquid is ruptured by means of a beam of elementary particles such as a neutron beam.

1.4.2.2 Sono-chemistry

Sono-chemistry is the use of cavitation energy to undertake and/or accelerate a chemical reaction. The cavitation energy can be used to provide high levels of heat (5000°C) and pressure (500 atm) as well as rapid rates of cooling ($10^9$ K/s) (Suslick 1990). The effects in chemistry are diverse and include super clean highly reactive surfaces from high speed jet impact, high speed impact of particles changing particle surface morphology, reactivity and composition and rate increases in stoichiometric and catalytic reactions (Suslick 1989; Suslick 1990; Mason 2000; Birkin et al. 2003). The majority of sono-chemical reactions are powered by acoustic irradiation, however splitting of particles such as biological cells is commonly achieved by hydrodynamic cavitation.

1.4.2.3 Acoustic cavitation in a bulk liquid

When ultrasonic irradiation is passed through a homogeneous liquid the expansion cycles exert negative pressure on the liquid. The negative pressure can pull the molecules away from one another and if the ultrasound is sufficiently intense then a cavity may be formed in the liquid. A cavity occurs when the negative acoustic pressure exceeds the tensile strength of the liquid. Normally cavitation is a nucleated process as it occurs at pre-existing weak spots within the liquid. The weak points tend to be at points of gases within the liquid, gas-filled crevices within suspended microparticles and transient microbubbles from prior cavitation events.
Once formed, a gas bubble will absorb energy from the sound waves and grow. The rate and mechanism of growth is dependent on the intensity of the sound. At high intensities a small cavity will grow rapidly due to inertia effects as cavity expansion is significantly rapid during the expansion cycle to not allow time to recompress during the compression cycle.

At low intensities the bubble will grow slowly with each negative pressure wave via a process called rectified diffusion (Figure 1.6). As it grows a small amount of gas or vapour will diffuse into the bubble from the liquid depending on the surface area. During positive pressure cycles the amount of gas/vapour leaving the bubble is less than the amount that entered during the negative pressure cycle. The result is a net gain in bubble size. Thus, over many acoustic cycles, the cavity will grow. The growing cavity can eventually reach a critical size where it can efficiently absorb energy from the ultrasonic irradiation. The size (resonant size) is frequency dependent and causes rapid growth of the cavity during a single acoustic cycle.

Eventually cavities exposed to either high or low intensity irradiation will grow to an unsustainable size. Once growth to this point is reached it can no longer efficiently absorb energy from the ultrasonic radiation. Without the energy input the cavity becomes unstable, the surrounding liquid rushes in and the cavity implodes completing the cavitation cycle.
Figure 1.6 The effect of negative and positive acoustic pressure on the formation, growth and implosion of bubbles in ultrasonically irradiated liquid (Suslick 1994)

1.4.2.4 Acoustic cavitation occurring near a solid surface
The dynamics of an ultrasonic cavitation bubble collapse are significantly changed when it occurs next to a solid surface. It is widely held that the mechanism of bubble collapse close to a solid boundary layer involves an asymmetric collapse via a liquid jet through the bubble interior. Fluid mechanics and high speed cinematographic photography have been used to propose the method of bubble collapse within an ultrasonic environment next to a flat solid surface (Lauterborn and Bolle 1975; Crum 1979; Lauterborn and Vogel 1984). Both works are only theories based on observations made in an environment similar to ultrasonic irradiation as cinematographic capture of the growth and collapse of a cavitation bubble in the presence of ultrasonic irradiation has not yet been published. In one of the published articles bubble
collapse was simulated by low frequency oscillation under reduced pressure (Crum 1979) whereas the other created cavitation bubbles with the aid of a laser (Lauterborn and Bolle 1975).

The first publication (Crum 1979) found that when a liquid is held at reduced pressure (at least 1 atm) in a container that was oscillated over a small amplitude (2-3 mm) at a low frequency (60 Hz) then a stable bubble was formed that would go through cyclic non-self destructing jetting. The jets had the same frequency as that of the driving amplitude and were large (1-3 mm in diameter) and periodic in nature to allow examination with modest photographic equipment. Figure 1.7 shows the sequence of bubble collapse captured by Crum as part of this work. The bubble is initially round, however as the vessel displaces in the direction of the surface the bubble grows in length and becomes oval in shape in the region of low pressure above the bubble. On a change in direction of the vessel the bubble returns to a spherical shape. However, the momentum of the liquid following the bubbles changes in shape, which forces a jet of water to pass through the centre of the bubble. As the pressure caused by the vessel movement returns to zero then the bubble also regains a spherical shape ending the sequence. Figure 1.8 shows a higher resolution image of a single bubble from the sequence shown in Figure 1.7. This image clearly shows the jet of liquid passing through the bubble towards the surface of the vessel.

The second work (Lauterborn and Bolle 1975) confirmed the asymmetrical collapse through the centre of the bubble and was able to determine microjet velocity (400 km/hr) from the images captured by high speed micro-
cinematographic sequence (Figure 1.9). The bubble collapse was observed to be asymmetric with the potential energy of the expanded bubble converted into the kinetic energy of a liquid jet that passes through the centre of the bubble and impacts the surface at a perpendicular angle to the surface. The energy of this impact can cause damage to the surface including removal of the surface. This phenomenon is seen in cavitation failure of an impeller blade where the metal surface is eaten away by each successive cavitation event until the structure fails.

Figure 1.7 A 60 Hz bubble collapse sequence next to a solid surface filmed at 5000 frames per second (Crum 1979)
Figure 1.8 An individual bubble showing jetting taken from the sequence shown in Figure 1.7 (Crum 1979)

Figure 1.9 Laser-induced cavitation near a solid surface (Lauterborn and Bolle 1975).
1.4.3 Ultrasonic Equipment

There are a number of devices that can be employed to provide ultrasonic irradiation to a liquid. The ultrasonic bath and ultrasonic horn are the common ways of providing acoustic energy to a bulk liquid and are used for cleaning purposes. Both use a transducer to impart high frequency sound waves to a liquid. Both piezoelectric and magnetostrictive transducers can be used to provide sound energy to a liquid.

High-pressure, high-speed and orifice plate homogenisers employing hydrodynamic cavitation are found extensively in industry but will not be expanded on here as they have little relevance to cleaning of surfaces due to the geometry of their cavitation chambers.

1.4.3.1 Magnetostrictive transducers

Magnetostrictive transducers were the first devices used for providing a robust supply of power for ultrasonic irradiation. The transducer works by applying an alternating magnetic field to a magnetostrictive material strip (such as nickel) that is connected to the side of the ultrasonic device. The limitation of this type of transducer is its size, energy conversion efficiency and low working frequency (less than 20kHz) (Fuchs 2001).

1.4.3.2 Piezoelectric transducers

Piezoelectric transducers initially were not a stable source of ultrasonic energy due to the fragile nature of the naturally occurring piezoelectric materials (quartz crystals and barium nitrate) that were used in initial transducers. Significant advances have been made in piezoelectric materials making piezoelectric transducers the most stable source of ultrasonic irradiation for ultrasonic bath style applications over a wide range of resonance frequencies.
Piezoelectric transducers work because a piezoelectric material changes dimensions when an electrical charge is applied to it. The piezoelectric material is sandwiched between a solid back mass and a coupling mass which is attached to the side of an ultrasonic bath, or a radiating surface submerged in the bath or against an amplifying device (ultrasonic horn). The piezoelectric material is fed with an alternating energy source that causes the expansion and contraction of the material which radiates into the bath through the radiating surface. Figure 1.10 shows the geometry of a piezoelectric transducer.

![Piezoelectric Transducer](image)

**Figure 1.10** Piezoelectric transducer

**1.4.3.3 Ultrasonic Bath**
An ultrasonic bath can be constructed in a variety of ways. The most common of these is that found in most laboratories for the purpose of cleaning. These baths are a thin wall stainless steel device with piezoelectric transducers attached to the base and/or sides. Irradiation can be provided at a fixed frequency, frequency scanning around a fixed frequency and at a number of frequencies depending on the transducers and power supplies used. Baths can have options including temperature, exposure time and power control. Size of
the bath, wall thickness, fluid level and placement of the transducers greatly affect the power level and irradiation transmission distribution within the bath. Figure 1.11 shows the geometry of a simple ultrasonic bath.

![Ultrasonic bath diagram](Image)

**Figure 1.11** Four transducer piezoelectric ultrasonic bath

### 1.4.3.4 Ultrasonic horn

An ultrasonic horn utilises an ultrasonic emitting transducer coupled to a metal device that amplifies the intensity of the standing wave from the transducer at the liquid interface. Figure 1.12 shows the geometry of a stepped ultrasonic horn. The horn acts as a strain amplifier and the level of amplification in a stepped horn is a function of the square of the diameter ratio (Sherrit *et al.* 2004). Horns are designed to work at one frequency only and are tuned in length to match the frequency of the transducer. The intensity of a horn can be controlled by changing the input energy for the transducer.
1.4.4 Ultrasonic Cleaning
There are two main methods for the cleaning of a surface from an aqueous environment and these are:-

- Chemical dissolution or emulsification of soluble contaminants
- Physical detachment of non-soluble contaminants

For contaminant removal to occur the cleaning chemistry must come into contact with the contaminant in order to promote removal. In an aqueous environment the cleaning chemistry is transported to the contaminated surface by water. After the contaminant is dislodged from the surface it is transported away in the same water. There must be an efficient transfer of the cleaning
chemistry to the surface and contaminants away from the surface for cleaning to occur. In ultrasonic irradiated cleaning this transfer can occur in two ways; micro-streaming resulting from cavitation bubble oscillation and micro-jetting caused by cavitation bubble implosion (Fuchs and Puskas 2005).

Chemical dissolution rate is controlled by the amount of solvent present at the contaminant surface. If there is a stoichiometric excess of contaminant with respect to the solvent then several refreshes of the solvent will be needed to effect dissolution. A viscous boundary layer is present along the surface of the contaminated item that restricts the movement of contaminated solvent away from the surface and limits the replenishment of fresh cleaning solution. The boundary layer is present even in a system with a turbulent flow of cleaning liquor near to the surface (Figure 1.13). For cleaning to occur the contaminant and cleaning solution must undergo diffusion through the boundary layer.

![Figure 1.13 Boundary layer of a surface with turbulent liquor flow](image)

The viscous boundary layer was estimated as being in the order of 30 µm for a surface that is not subjected to ultrasonic irradiation (McQueen 1986). The introduction of ultrasonic irradiation reduces the thickness of the viscous boundary layer as its thickness is inversely proportional to the square root of the frequency (Morse and Ingard 1960). A surface subjected to ultrasonic
irradiation at 30 kHz has a 4.4 µm viscous boundary layer whereas one subjected to 900 kHz has one of ≈0.8 µm.

Other work (Bulat 1974) confirms the boundary layer reduction but describes the ultrasonic effect on a surface as maximising the cleaning chemistry at the surface of the item being cleaned. This publication suggests that the cleaning action is from the dislodgment or dissolution of contaminants from the surface due to the micro-jet effect during cavitation. The dislodged water soluble components are then easily emulsified during cavitation and insoluble components are pulled away from the surface and dispersed in solution. Particles can be directly dislodged by one jet or by a series of jets fatiguing the bonds that holds them to the surface. A cleaning effect of micro-scrubbing is achieved by the oscillation of cavitation bubbles before implosion against the contaminated surface.

Figures 1.14 and 1.15 show the difference between a system with and without ultrasonic irradiation. In Figure 1.14 the boundary layer provides the limiting rate of cleaning as the clean and saturated cleaning liquor must diffuse over this boundary layer to be removed from the surface. In Figure 1.15 the thickness of the boundary layer is significantly reduced due to the presence of ultrasonic cavitation within the bath increasing the diffusion rate. Cavitation events close to the surface cause accelerated dissolution of the contaminant and disruption of the boundary layer in the vicinity of the cavitation collapse (Bulat 1974). The same research extends this theory to non soluble particle removal by mechanical detachment by cavitation events next to the particle and close to the surface.
1.4.4.1 Processing parameters
The main processing parameters that affect ultrasonic cleaning are frequency, intensity and transmission.

1.4.4.2 Frequency
There are three main theories about the ultimate frequency for cleaning and these works have been expanded on below.

One theory is that a surface contaminant is either microscopic or sub-microscopic (McQueen 1986). With microscopic particles, the number of bonds retaining a contaminant on the surface is high and they need to be broken before the particle can be dislodged. The high energy of a single cavitation bubble collapse of low frequency ultrasonic irradiation is enough to
dislodge the particle in a single step whereas multiple bubble collapses would be needed in a high frequency system. Even with multiple bubble collapses, the high frequency ultrasonic irradiation may not remove macroscopic particles as the time between each collapse is long, allowing reattachment of the binding bonds thus thwarting detachment.

With sub-microscopic particles the number of bonding sites must be less and hence detachment with small energy is possible however research suggests that it is not the shear force acting on the particle that sponsors detachment from the surface as the particles are deeply buried in the viscous boundary layer of the cleaning solution (McQueen 1986). The mechanism of particle removal is related to solvent nature and its effect on chemical equilibrium of detachment. A higher frequency of ultrasonic irradiation is more effective than a lower frequency as the boundary layer is thinner for high frequency irradiation. A thinner boundary layer facilitates a higher turnover of solvent at the surface being cleaned and subsequently the rate of particle removal is increased.

A second theory suggests that the size of the cavitation bubble influences the level of cleaning undertaken on a surface (Fuchs and Puskas 2005). For cleaning to take place the cavitation bubble needs to form and catastrophically implode next to the surface. If the bubble was to grow in a confined space it could not reach a size where it could implode and would either not form, or oscillate and degenerate without imploding. As frequency controls cavitation bubble size, a higher frequency is more likely to clean a surface with fine
surface detail or small contaminant particle size. Figure 1.16 shows the relationship between bubble radius and frequency.

![Figure 1.16 Cavitation bubble size with reference to frequency (Fuchs and Puskas 2005)](image)

A third theory suggests that a low frequency (20kHz) is the best alternative for cleaning as the cavitation bubble is larger and hence its subsequent collapse produces higher energies and stronger micro-jetting (Bulat 1974). At low frequencies the time taken between positive and negative acoustic waves is longer hence there is more time for bubble growth. Low frequency ultrasound has greater penetration power and provides better penetration into large items or interstices. High frequency cavitation did not have the penetration power to provide adequate cleaning in a large cleaning system.

1.4.4.3 Frequency scanning
Working at a fixed frequency can cause high and low intensity points within an irradiated bath due to additive and subtractive wave theory. Frequency
scanning of 1 – 2 kHz around the irradiation frequency via frequency scanning helps to even out the distribution of irradiation intensity, within a bath, over a period of time. Working at two or more frequencies can also maximise contaminant removal as both a low and high frequency irradiation can be pulsed in series to a cleaning system (Fuchs 2001; Puskas and Piazza 2001).

1.4.4.4 Intensity
The amplitude (power) of a standing wave is important in the creation of a cavitation event within a liquid. It has been stated that the minimum power needed to initiate cavitation is 1/3 W/cm² (Strasberg 1959) with cavitation increasing proportionately to power. If power is increased too high then heavy cavitation will be produced at the transducer face. This produces a large number of cavitation voids and gas pockets which impede sound waves from travelling further into the cleaning tank (Bulat 1974).

1.4.4.5 Transmission
Transmission of the ultrasonic irradiation evenly throughout the ultrasonic bath is important in creating a reproducible technology for wool cleaning. When a wave meets a boundary between two media it is partially reflected, absorbed and transmitted. Nearly all materials placed into the path of an ultrasonic waveform travelling through a liquid will absorb. The energy absorbed from the wave is converted into heat. The level of adsorption is governed by the acoustic characteristics, amount and spacing of the material within the liquid. A large amount of work has been conducted on quantifying the degree of absorption/transmission of a textile fabric in an ultrasonic bath at 25 and 40kHz (Datar et al. 1996a; Datar et al. 1996b). A wide range of fabrics were studied including cotton, polyester, nylon, acrylic, polypropylene, polyethylene
and glass. It was found that the transmission of ultrasound through a fabric decreases as the fabric weight increases. An increase in irradiation frequency resulted in reduced transmission. The fibre type showed slight differences with cotton having the lowest transmission and synthetics having the highest. It was proposed that the hairiness of the cotton fabrics resulted in less space for transmission. Fabrics were seen to absorb very little ultrasonic irradiation with most being either reflected or transmitted. The level of wetting of the fabric had the highest influence on transmission with 50% transmission for a poorly wetted fabric and almost 100% transmission for a thoroughly wetted fabric (Datar et al. 1996b). The level of wetting normally refers to the presence of air on the surface and within the structure of the fibre. Cotton is not a homogeneous fibre like a synthetic. The structure provides many cavities where the presence of minute air pockets may occur on the fibre surface and within the fibre. Most synthetic fibres are closely packed in their structure and have smooth surfaces and hence the presence of air pockets is significantly reduced. The presence of air reduces the transmission of an ultrasonic wave through a medium.

1.4.4.6 Ultrasonic energy measurement
There are many ways to measure the ultrasonic energy that is applied to a liquid by a transducer. The most common tests used to evaluate power include measuring acoustical power, chemical activity, calorimetric change in temperature and erosion of a known solid item. Each of these is expanded on below.
1.4.4.6.1 *Acoustical power*

Acoustical power within an ultrasonically irradiated bath can be measured by immersion of a piezoelectric hydrophone into the bath. The hydrophone horn is able to measure both acoustical pressure and cavitation noise. Measuring the acoustical pressure in a confined space will give a similar acoustic pressure at several locations within the bath as it tends to distribute itself evenly throughout the bath. The measurement of acoustic pressure over time is a valuable tool to evaluate the efficiency of a bath as the acoustic pressure will fall as the unit power degrades (Bulat 1974).

Although hydrophones give a numerical value against ultrasonic energy the information gathered is not easily compared with other systems. Placement of the hydrophone is extremely important as acoustic pressure and cavitation noise vary within the bath depending on transducer placement. The hydrophone only measures one small point within the bath and without multiple measurements in multiple locations cannot be used to describe the cavitation behaviour of the whole bath (Bulat 1974).

1.4.4.6.2 *Chemical activity*

A range of sono-chemical accelerated reactions can be used to measure the level of activity within a bath. The spectrophotometric or electrochemical measurement of a reaction species is conducted versus time to determine the level of ultrasonic cavitation. Most reactions are sensitive to a range of factors including ultrasonic energy and due to this, repeatability of chemical measurement is poor (Bulat 1974). Common reactions like the conversion of
iodine salts into free iodine, the rate of production of hydrogen peroxide and degradation of the organic dye amaranth have been used (Birkin et al. 2003).

1.4.4.6.3 Erosion of a solid

Placing a piece of metal into a bath of known mass can be used as an evaluation method for ultrasonic cavitation. The ultrasonic irradiation will cause a series of pressure changes at the surface of the metal which are capable of cold working the surface (Bulat 1974). A thin piece of metal foil placed within an ultrasonically irradiated bath will produce dimples followed by perforations. These perforations can be estimated for size using light transfer (Crawford 1964) and visual assessment. The use of a piece of foil is very useful in determining the regions of cavitation within a bath. A large piece of solid metal, such as lead, of known mass can also be used and the amount of metal removed over a period of time is used to determine the amount of cavitation. This method is not often used due to its poor reproducibility (Crawford 1964; Bulat 1974).

The foil method is the most frequently used for cavitation evaluation and is quoted to be the most accurate method for determining entire bath cavitation performance (Crawford 1964). Accuracy is due to the ability to place the foil over a wide span of the bath. The erosion measured is averaged over a large area hence it represents multiple points within the plane of the bath. Multiple plane measurements should still be made for an entire picture of the baths ultrasonic characteristics.
1.5 Textile and Fibre Ultrasonic Applications

A wide range of applications have been undertaken using ultrasonics in the presence of a textile fibre. This work includes elastic moduli, fibre disintegration, bast fibre separation, chlorination, raw wool fibre scouring, garment cleaning, scouring, desizing, bleaching, enzyme treatment, chemical coating, nonwoven consolidation and heat treatment. Heat treatment includes thermofixation, embossing, bonding, slitting and cutting.

A large amount of work was conducted into the absorption of ultrasound by fabric (Datar et al. 1996a; Datar et al. 1996b). Both high and low intensity ultrasonic irradiated systems were investigated as power transmission measurement accuracy was lower in the presence of cavitation events. Low frequency irradiation showed that the level of fibre wetting was important to the level of transmission of ultrasound through a fabric. Low levels of wetting restricted ultrasound whereas good wetting provided almost 100% transmission of ultrasound through the single layer of fabric. The importance of fibre wetting is confirmed by others (Gallego-Juarez et al. 2009) and should be considered with all ultrasonic applications.

1.5.1 Fibre Disintegration

Ultrasonic agitation has been used by many researchers for the disintegration of fibres for chemical and microscopical analysis. This process is not limited to fibre type, however the technique has largely been used for natural fibres including cotton, cellulose solutions, wool and silk. In most cases high ultrasound power density and/or small fibre masses were used to achieve full or partial disintegration.
A large amount of work has been conducted on the disintegration of wool fibres for microscopical analysis (Bradbury and Chapman 1964; Bradbury and Peters 1972; Bradbury 1973). Ultrasonic disintegration has also been utilised to reveal the micro-fibrilar structure of a jute fibre under scanning electron microscopy (Mukhopadhyay et al. 1985).

In 1954 the Newsletter for Wool Textile Executives (Effect of Ultrasonic Energy on Fibrous Materials 1954) gave a description of the effects of ultrasonic energy on various fibrous materials. The work involved the frequencies of 10, 22, 30, 80 and 175 kHz in distilled water. 10 kHz caused the highest damage with the degree of damage inversely proportional to the frequency of the ultrasonic vibrations. Cellulosic fibres exhibited large damage after short exposure to ultrasonic agitation whereas wool was resistant to damage even after long exposure with only partial removal of the scale structure after 30 minutes.

Research used 700kHz for a duration of 20 minutes to partially disintegrate 5-150 mg wood pulp, cotton, ramie and rayon before and after acid hydrolysis (Morehead 1950). This experiment was conducted at low temperatures as the ultrasonic vessel was chilled by circulating ice water. Ultrasonic agitation in distilled water alone caused fibrillation of part of the cellulose sample into long and short fibrils of 200-400 nm. These findings (Morehead 1950) are the opposite of the results of another researcher (Martin 1953) who found that, at the working frequencies of 400, 500 and 800 kHz (400 watts) and 10 minutes irradiation of 15 g samples, there was no fibrillation or chemical damage occurring to cotton lint. Temperatures of the work did not exceed 80°C at the
end of the irradiation. The main difference in the work was the frequencies used and the size of the samples. The power intensity provided to irradiate the fibre may also have been a contributing factor to the differences in the experiment however Morehead did not publish the power used.

The disintegration of fibres has been utilised for the production of nano-fibres from natural materials (Zhao et al. 2007). This study examined animal fibres including silk and spider silk along with a range of cellulose based materials. The approach was to use high intensity sonication at a frequency of 20 kHz. A very small sample of material (e.g. 0.05 g silk) was placed in 100 ml of water and sonicated for extended periods of time (30-45 min) with intensities reaching 900-1000 W. Once again very high intensity irradiation is used to achieve the disintegration.

Others observed scale damage or scale removal after low frequency irradiation (20 kHz) at moderate power levels (600 W) (Mao et al. 2005). One research publication found disintegration was assisted by the closeness of the fibre to the transducer as the non-woven fabric being irradiated was sandwiched between the transducer and a flat metal plate at a pressure of 200 Pa (Zhao et al. 2007). This has the same effect as increasing the power density within the bath hence increasing the level of disintegration. The level of disintegration was also increased by increasing the concentration of anionic surfactant and pH.

1.5.2 Bast Fibre Separation

A number of researchers have utilised the energy of ultrasonic irradiation in the separation of bast fibres (Hurren et al. 2004; Wang and Wang 2004). The
process used was a modified aqueous chemical retting of the bast fibres in the presence of ultrasonic irradiation, temperature, alkali and detergent. The ultrasonic irradiation is used to promote penetration of the retting liquid within the fibre bundles. The authors found that cavitation close to the fibre bundle surface increased the mechanical separation of the fibres due to liquor jet impingement on the fibre surface and at the fibre to fibre junction.

1.5.3 Chlorination
The use of ultrasonic irradiation for the purposes of improving the chlorinated shrink resist processing of wool fibres has been investigated (Khajavi and Azari 2007). The work proposes that the rate of chlorination is increased however the mean percent shrinkage results quoted show the ultrasonically chlorinated fibre has higher shrinkage than the control sample and there are not enough microscope images to determine if the surface morphological changes are consistent throughout the treated sample.

1.5.4 Raw Wool Fibre Scouring
Very little work has been undertaken in ultrasonic assisted scouring of raw wool. One publication examined the scouring of wool with ultrasonic irradiation at a frequency of 25 kHz at different temperatures and detergent levels using progressively reduced number of scouring baths (Cui 1999). This work found that ultrasonic agitation was able to achieve quality scoured wool with a reduced scouring time at a lower temperature, or reduced amount of detergent in comparison with that required by the conventional aqueous scouring. Some rounding of the fibre scale tips were observed but no other changes to the cuticle structure were noted (Cui 1999).
1.5.5 Garment Cleaning
The cleaning of textile structures has been undertaken in various forms using ultrasonic agitation. Most of the work has been based around cleaning of fabric to simulate fabric in a garment (McQueen 1986; Warmoeskerken et al. 2002), garments (Memberg and Memberg 1996; Horning 1998; Canoglu et al. 2004) and fabric structures.

The frequency dependence of ultrasonic cleaning of fabrics was investigated for the removal of blood stains from cotton cloth using 40 and 220 kHz (McQueen 1986). The author found that the limiting factor of the cleaning process was in the initial destruction of the blood clot. Low frequency ultrasonic irradiation provided more energy in the destruction of the blood clot and hence provided the best cleaning effect. The higher frequency ultrasonic irradiation had a negligible effect on the removal of the blood clot when compared to the control sample.

One publication focused on improving the mass transfer within a fabric structure (Warmoeskerken et al. 2002). The experiments used 33 kHz ultrasound to irradiate a cotton swatch that had been soaked in a salt solution. Conductivity measurements versus time showed that the mass transfer rate is up to six times faster for ultrasonically irradiated rinsing when compared to squeezing the structure to promote liquid transfer. This work was extended to examine the convective diffusion coefficient which was proposed as the limiting factor in removing a particle contaminant from a textile (Moholkar and Warmoeskerken 2004). The authors found that higher acoustic pressure amplitudes gave higher diffusion coefficients at an irradiation frequency of 25 kHz.
Extensive work has been conducted to determine the mechanism of cleaning on the surface of a textile substrate (Moholkar and Warmoeskerken 2003; Moholkar and Warmoeskerken 2004; Moholkar et al. 2004). As seen from the previous paragraph it was determined that it was the diffusion coefficient of a contaminant away from a fibre surface that is improved in ultrasonically assisted cleaning. This improvement in diffusion coefficient was due to cavitation bubble collapse and cavitation bubble induced micro-streaming and not the ultrasound wave (Moholkar et al. 2004).

The removal of blood stains on polyester, polyester/cotton (65/35%) and polyester/carbon (99/1%) surgical gowns has been studied with 47 kHz ultrasonic irradiation (Canoglu et al. 2004). The authors found that irradiation had an improvement in blood clot removal for all fabrics however the ultrasonic irradiation had moderately deleterious effects on the tenacity of polyester fabrics. The tenacity loss was not observed in the other fibre blends and the reason for strength loss was not investigated.

There have been two attempts by research groups in the USA to develop a commercial process for cleaning textiles. Both David Porter (Memberg and Memberg 1996) and later Thomas L. Hoffmann of the Fraunhofer Technology Centre (Horning 1998) announced a proposal to develop an ultrasonic assisted commercial cleaning process for garments. No further information has been published on their work.

Research found that 300 W, 50 kHz ultrasonics assisted in the cleaning of dairy fouled ultra-filtration membranes at temperatures from 25°C to 55°C (Muthukumaran et al. 2005). Cleaning efficiencies of 5-10 % were achieved by
suspending the membrane in a specially designed bath and ultrasonically irradiating it during the cleaning cycle.

1.5.6 Scouring, Desizing, Bleaching and Enzyme Treatment
Industrial processing of fabrics, including pre-treatment and bleaching, lend themselves to sono-chemical acceleration from ultrasonic irradiation. Most are carried out with a series of chemicals, detergents, oxidants and enzymes that are assisted in their action by good fibre liquor interaction. A number of researchers have investigated ultrasonically assisted work on a range of different fibres including desizing/scouring (Goodman and Hilton 1963; Yachmenev et al. 2002; Yachmenev et al. 2004; Fakin et al. 2005; Karaboga et al. 2007; Gallego-Juarez et al. 2009), bleaching (Fakin et al. 2005; Mistik and Yukseloglu 2005) and bio-finishing (Yachmenev et al. 2002; Yachmenev et al. 2004).

Early investigations into the use of ultrasound in textiles found few technologies had been developed for production with only the Rapiclean tank (Ultrasonics Ltd) designed for open width fabric cleaning described (Goodman and Hilton 1963).

Work was conducted on bleaching of cotton fibres, yarns and fabrics using an ultrasonic bath at 20 kHz (Mistik and Yukseloglu 2005). The work compared bleaching in the presence of ultrasonic agitation at low temperatures (20, 30 and 40°C) with varied times (20, 30 and 60 minutes) with conventional bleaching at 90°C for 60 minutes. Whiteness values for the ultrasonically agitated experiments were not as high as the conventional bleaching, however
the results were inconclusive as a conventional bleaching at the lower temperature was not supplied for comparison.

It was found that enzymatic scouring and bleaching of flax fibres in the presence of ultrasonic irradiation was better than alkali and acidic ultrasonic assisted scouring and bleaching (Fakin et al. 2005). The whiteness values were higher that the control sample, however fibre tenacity was sacrificed.

Other bleaching work (Basto et al. 2007) found that the supply of low energy ultrasonic agitation (20 kHz and 7 W) intensified the enzymatic process of laccase bleaching.

Ultrasound irradiation at 16 and 20 kHz in a parallel plate near field acoustical processor can provide an increase in enzyme activity so that reduced enzyme concentrations can be used (Yachmenev et al. 2002). This minimises cost and effluent contamination. Work covered the enzyme treatment of cotton fabric during desizing, scouring, bleach clean up and bio-finishing. Further work proposed that it was both mass transport to and from the fibre surface along with enzyme catalysis from ultrasonic irradiation that improved the process (Yachmenev et al. 2004). Similar results were observed when treatment was done in the presence 25 kHz ultrasound from an ultrasonic bath (Karaboga et al. 2007). They proposed that the improvement was from liquor exchange at the fibre surface and achieved reduced use of chemicals and enzymes for the same level of treatment.

The batch wise processing of a fabric in a jig dyeing machine is considered to be semi-continuous. Laboratory trials with a laboratory scale jig at 24 kHz for
the removal of lubricants and size from the surface of polyamide and cotton fabrics have been published (Vouters et al. 2004). The authors proposed that an industrial machine would see savings in dye and chemical consumption, effluent reductions (20-30%), water use reduction (20%), energy reduction (30%) and a 20% improvement in product quality.

All of the previous treatments have been batch processes whereas a continuous process designed for the continuous washing of open width fabric has been proposed (Gallego-Juarez et al. 2009). The work is novel due to the special design of a 20 kHz ultrasonic horn with plate face developed and patented by the researchers. Improvements in cleaning efficiencies are similar to those seen in previous work however the volume of the irradiation bath is significantly reduced so liquor and effluent volumes would also be significantly reduced compared to other processes.

1.5.7 Chemical Coating
Sono-chemistry can be used as an alternative to high speed mixing as a way to create nanoparticles. The disruption of the cavitation events stops the formation of large agglomerations of molecules when preparing a nanoparticle dispersion. Research utilised a sono-chemical driven reaction to form silver nanoparticles on the surface of merino wool fibres (Hadad et al. 2007). No changes to surface morphology were observed but it was proposed that micro-jetting during cavitation collapse next to the fibre surface caused an acceleration in the nanoparticle that made it impact with the fibre surface. The impact would embed the particle within the fibre surface structure providing
better bonding with the surface, however they did not provide microscopic proof of this phenomenon.

Ultrasonic irradiation during the application of other chemicals would be expected to accelerate the application of these chemicals due to the improvement of mass transfer of the chemical to the fibre surface. This effect has been observed in the improved pickup of a cationic softener onto a cotton fabric with 30 kHz ultrasound (Parvinzadeh et al. 2010). Improvements in bending angle, surface friction and colour were observed, however the level of softener used was five times more than what would normally be used in industry so exact benefits cannot be inferred from the results.

1.5.8 Nonwoven Consolidation
Nonwoven consolidation is conducted to cause binding of fibres within a nonwoven structure and changes in fabric morphology (thickness, surface appearance, etc). Low frequency ultrasonic irradiation (20 kHz) was utilised on a piece of nonwoven wool fabric sandwiched between the transducer and a flat metal plate to undertake consolidation and surface modification (Mao et al. 2005). The work showed that ultrasonic irradiation at acidic pH resulted in area shrinkage (35 %) and thickness increases (40-50 %) whereas irradiation at neutral and alkaline pH produced no change or small increases in fabric area dimensions (0-10 %). High intensity ultrasonic irradiation at such a close proximity to the fibres caused high levels of fibre cuticle fracture and cuticle removal. Cuticle removal was increased with increasing surfactant concentrations and pH. Fibres on the surface of the transducer and metal plate underwent higher levels of damage than those buried in the body of the fabric.
as cavitation was higher at the transducer surface and at the reflection point on the metal plate. Direct interaction between the fibre and the moving plate may also have been responsible for the higher levels of damage but this was not suggested by the authors.

1.5.9 Heat Treatment
The use of ultrasound has proven popular in the heat treatment of synthetic polymers. High intensity, low frequency (20-35kHz) ultrasonic irradiation of a textile fibre within a confined space in air will cause a rapid heating of the fibre. The use of ultrasonic irradiation in this manner is used to undertake heat related processes on dry synthetic fibre matrices. The nonwoven industry utilises this energy to enable lamination, embossing, cutting, welding and slitting. Other synthetic fabric treatments include thermo-fixation, hole cutting, welding and edge binding.

1.5.9.1 Nonwoven production
A number of industrial applications have been developed to enable processing of nonwoven textile materials. Hermann Ultraschalltechnik GmbH & Co. KG of Karlsbad Germany have developed a range of ultrasonic processing equipment to enable continuous embossing, bonding, slitting and cutting (Nonwovens - Continuous lamination, embossing, slitting and cutting of roll goods 2006). They claim that their non-contact technology enables wear free processing of webs without heat or thermal distortion. The compression of the textile between the vibrating sonotrode and a fixed anvil drum provides the energy to produce the weld or slitting. The absence of heat on the embossing device means that production can be stopped and started without product waste or product nonconformity.
1.5.9.2 Thermo-fixation
Sonotronic Ultrasonic Technology of Karlsbad, Germany have developed a thermo-fixation device for processing tape and ribbon (Treatment of textiles 2007). The device utilises the rapid heat up rate provided by ultrasonic irradiation to raise the synthetic tape to a temperature capable of heat setting. The rapid rate of temperature rise reduces the machine size and energy consumption.

1.5.9.3 Welding
A number of companies provide equipment that is capable of welding (laminating) a synthetic material (Schips : Sewing and ultrasonic technology 2007; Treatment of textiles 2007). The technology works on the same principle as heat setting however the distance between the sonotrode is shorter.

1.5.10 Ultrasonic Dyeing
A number of factors have been proposed for the improvement of dyeing by ultrasonic irradiation. Most researchers propose that the increase in dyeing rate is due to particle size reduction of the dye (El-Shishtawny et al. 2003; Kamel et al. 2003; Lee et al. 2003; Kamel et al. 2005; Ahmed et al. 2007; Kamel et al. 2007; Vankar et al. 2007; Vankar et al. 2008; Kamel et al. 2009), however mass transport (Munteanu et al. 2007; Fakin and Ojstrsek 2008), fibre swelling (Vankar et al. 2008), improved dye diffusion (El-Shishtawny et al. 2003; Kamel et al. 2003; Kamel et al. 2005; Ahmed et al. 2007; Kamel et al. 2007; Fakin and Ojstrsek 2008; Kamel et al. 2009) and fibre surface modification (Kamel et al. 2009) have also been proposed.

Some improvement in dye uptake on nylon (microfibre)/Lycra blends for CI reactive blue dyes 4, 15 and 52 was observed, however most showed more dye
removal during subsequent washing and only small improvements in perspiration fastness only (Merdan et al. 2004). Frequencies and power were not quoted.

The use of ultrasonic irradiation from an ultrasonic bath (28 kHz, 154 W) in assisting low temperature dyeing of poly(ethylene terephthalate) was undertaken (Lee et al. 2003). The work found that some disperse dyes were assisted and some were not and that reduction in dye molecule agglomeration within the bath provided the mechanism for dye penetration.

A number of works on the dyeing of cotton, wool and silk with natural dyes in an ultrasonic bath (20 kHz, 150W) have been published (Vankar et al. 2007; Vankar et al. 2008). Experiments observed increased rates of dye uptake and this was explained by enhanced dye diffusion due to increased fibre swelling and reduced dye agglomeration. Their work did not quantify fibre swelling or particle size changes.

An ultrasonic horn (20 kHz, 750 W) was utilised during the conventional and low temperature dyeing of flax fibres with disperse dyes (Fakin and Ojstrsek 2008). It was found that dyeing temperature could be lowered due to an increase in the diffusion of the dye into the fibre and an improvement in dye movement to the surface of the fibre.

A combination of ultrasonics (20 kHz and 6 W/cm²) and cyclic voltammetry was used to oxidise 2,2-Azinobis(3-ethylbenzothiazoline-6-sulfonate) ABTS to colour a wool fabric (Munteanu et al. 2007). The ultrasound was found to
assist in the colouration process by improving the mass transport of the ABTS$_{2+}$ species from the electrode to the surface of the wool fabric.

Reactive dyes were applied to cotton fabrics within an ultrasonic bath (40 kHz) and in a bath irradiated by an ultrasonic horn (20 kHz, 250 W) (Akalin et al. 2004). The work found that exposure during dyeing to an ultrasonic horn provided better dye exhaustion than the ultrasonic bath, however they made no reference to the mechanism or the effect of frequency or power.

Most papers published in the area of ultrasonic assisted dyeing are by one research group (El-Shishtawy et al. 2003; Kamel et al. 2003; Kamel et al. 2005; Ahmed et al. 2007; Kamel et al. 2007; Kamel et al. 2009) and a summary of this work follows in this paragraph. The work used an ultrasonic bath (38.5 kHz, 500 W) to undertake colouration on a range of different fibres including wool, cotton, nylon 6 and flax. They found that ultrasonics improved the dispersion of the dye within the dye-bath, removed trapped air pockets from the surface and from within the fibre, improved the fibre to dye interaction, improved diffusion within the fibre and an accelerated interaction or chemical reaction of the dye with the fibre. With nylon they found that dyeing rate was also improved by an increase in the crystalline regions of the fibre due to ultrasonic irradiation. In their 2009 work they found that the ultrasound had disrupted the surface of cotton fibres and felt that this may have contributed to increased pathways for penetration of dye into the fibre.
1.6 Problems, Gaps and Opportunities from the Literature

Ultrasonic cleaning is a proven technology for the precision cleaning of items in a number of industrial applications including assembly and medical fields. Many researchers have looked at utilising ultrasonic energy to enhance the removal of contaminants from textile fabrics in preparation for dyeing and finishing or for in service cleaning of textile products. Good work has been undertaken into the transmission of ultrasonics through a textile fabric (Datar et al. 1996a; Datar et al. 1996b) however this only extended to transmission through one layer of fabric and not multiple fabric layers or fibres within a bath. Good insight into the method of cleaning improvement within a textile fibre is published (Moholkar and Warmoeskerken 2003; Moholkar and Warmoeskerken 2004; Moholkar et al. 2004) with mass transfer from the fibre surface and within the cleaning bath determined as having the largest influence. Little work has been undertaken in evaluating the level of contaminant removal achievable in baths with liquor ratios similar to those used in industry or laundering. Few publications were found on the effects of dimensional stability or fabric property changes caused by ultrasonic irradiation.

A number of researchers have applied ultrasonics to textile fibres for the purpose of cleaning and colouration, however little work has been undertaken on wool with work being investigated in the areas of wool cleaning (Cui 1999), chemical coating (Hadad et al. 2007), non-woven consolidation (Mao et al. 2005) and wool dyeing (Kamel et al. 2005; Munteanu et al. 2007; Vankar et al. 2008). Two publications (Cui 1999; Mao et al. 2005) saw changes in the
surface morphology of the wool fibre however the effect of these changes on single fibre properties has not been further investigated. Many researchers have proposed that dyeing improvements in the presence of ultrasonic irradiation is due to improved dispersion of the dye within the dye-bath, removal of trapped air pockets from the surface and from within the fibre, improved fibre to dye interaction, improved diffusion within the fibre and an accelerated interaction or chemical reaction of the dye with the fibre (El-Shishtawy et al. 2003; Kamel et al. 2003; Kamel et al. 2005; Ahmed et al. 2007; Kamel et al. 2007). It is only recently proposed that improvements in cotton dyeing could be contributed to by an ultrasonic induced change of the surface morphology (Kamel et al. 2009).

1.7 Preliminary Studies, Key Hypothesis and Thesis Outline

The research in this thesis aims to answer the following three questions:

- Does the use of ultrasonic irradiation within a bath of water, wool and detergent improve the stain removal power of the bath and enable one or more of the following efficiencies: lower temperature, lower fibre entanglement and or less detergent?

- Does the use of ultrasonic irradiation of wool fibres affect fabric properties such as tensile strength, elongation to break, Martindale abrasion and pilling?
Does ultrasonic irradiation of a bath of water, wool and detergent have an effect on the structure and properties of the wool fibre – changing single fibre properties and increasing dye entry pathways?

To gain this understanding the work will be conducted in four parts. The first part of this work will examine greasy wool scouring and will investigate if improved process efficiency can be achieved using ultrasound. The second part of the work will look at fabric and determine the effect that ultrasound has on stain removal and fabric properties. The third part will determine if surface morphology changes will have an effect on single fibre properties and will aim to quantify what effect irradiation intensity has on surface morphology change. The final part of this work will investigate if surface morphology changes have an effect on dyeing rate of wool.
2 Ultrasonic Greasy Wool Scouring

2.1 Introduction

Wool scouring is one of the most important steps of early-stage wool processing. The objective of scouring is to remove contaminants such as grease, dirt, and suint (sheep sweat) from the wool, without damaging the fibre properties. The scouring method and technique applied have a direct effect on the quality of scoured wool (Anderson and Christoe 1984; Christoe 1986). Although many systems for scouring have been developed over the years, only two systems have gained wider use. These two systems are aqueous scouring and solvent scouring. Both systems have their advantages and disadvantages.

The most important process of aqueous scouring is emulsification of the grease on the fibre surface. The detergent, water, temperature and mechanical movement of the scouring liquor act to remove the contaminants from the wool. Aqueous scouring is usually carried out under conditions of high temperature (50°C plus) with a high detergent concentration. The process involves high consumptions of water and energy. Aqueous scouring systems currently in use include the WRONZ mini-bowl system, CSIRO condensed bowl system and the Fleissner Drum scour.

The process of solvent scouring involves the solvent dissolving the wool grease, however it is ineffective in the removal of wool suint, dirt, and proteinaceous matter. The equipment utilised for solvent scouring is complex and requires careful monitoring to maintain safe operation. Wool scouring solvents can be ozone depleting, toxic to humans and marine pollutants which
makes them hard to work with during wool scouring especially in the recovery of solvent after processing. These factors have combined to reduce the adoption of solvent scouring.

Most research in the area of wool scouring has focused on optimising aqueous scouring methods to improve the quality of the scoured wool (Stewart 1985; Bateup 1986; Christoe 1988; Stewart and Jamieson 1988; Smith 1989; Gutierrez 1999; Schafer et al. 2000; Poole and Cord-Ruwisch 2004). Ultrasonic irradiation has been used in many fields for the removal of grease and surface contaminants. Conventional non-ionic detergent wool scouring utilises aqueous scouring liquors, chemicals and conditions that are similar to those employed in ultrasonic cleaning. The use of ultrasonic irradiation during wool scouring should be simple to implement, however little has been reported on the application of ultrasonic irradiation during wool scouring.

Irreversible entanglement of wool fibre, better known as felting, is the largest factor impacting the quality, processability and appearance of a wool product after it has been washed (Blankenburg 1969). Wool felting during scouring reduces processing yields and mean length of processed fibres due to increased fibre breakage (Christoe 1986; Bateup and Christoe 1996). The mechanism of fibre felting is very complicated and findings reported in the literature are not always consistent. Felting is a form of tangling produced by the persistent migration of individual fibres in the tip-to-root direction, which is caused by the directional frictional effect of fibres (Mercer and Makinson 1947; Makinson 1964; Makinson 1979). Wool cuticle scale interlock limits fibre migration to one direction, making it an irreversible process. Fibre migration is increased significantly when the wool is placed in a warm, moist, lubricated environment in the presence of mechanical agitation (Brady 1997). These
conditions are found in most wool cleaning systems, with the detergent acting as the lubricant. Felting can be reduced if the mechanical agitation is reduced. However, liquid transfer through the fibre is also lowered, leading to less efficient cleaning. Ultrasonic irradiation produces a series of cavitation events within a bath promoting liquor transfer. Each cavitation event is not large enough to cause fibre migration however the chain of cavitation events link producing efficient dissolution and mass transfer.

Investigations into the use of ultrasonic irradiation of wool scouring liquors are reported in this Chapter. A number of factors have been investigated, which relate directly to wool quality and processability after the scouring process, and/or a reduction in the environmental impact of the scouring process. Four separate experiments are presented, each with its own experimental conditions, results, discussion and conclusions. The overall findings are summarised at the end of the Chapter. The first experiment examines the effect of detergent concentration and scouring bath temperature on ultrasonic scouring. The second experiment quantifies the reduction in fibre felting achieved by ultrasonic irradiation relative to mechanical agitation. The third experiment examines the effect of fibre loading within the scouring bath and its adsorption of ultrasonic irradiation. The fourth experiment examines the effect of fibre loading on grease removal, dirt removal and whiteness.

2.2 Detergent Concentration and Liquor Temperature

2.2.1 Experimental
2.2.1.1 Raw wool preparation
Two Merino wool fleeces were selected according to fibre diameter. One fleece had a mean fibre diameter of approximately 18 μm and the other 22 μm.
2.2.1.2 Scouring method
Each scouring experiment consisted of five sequential cleaning steps at a fixed temperature (either 50°C or 60°C) for three minutes duration in each step. Each step was conducted in a conical flask suspended within the ultrasonic bath or placed on the platform mixer. A fresh cleaning solution was used for each step. The first three steps contained the same level of detergent, Hydropol TN450 (Nonyl Phenol Ethoxylate detergent, Huntsman Chemicals), with four concentration levels examined (0.05, 0.125, 0.25 and 0.50g/l) along with a fixed concentration of 0.20g/l sodium carbonate (Sigma-Aldrich Co., USA). The last two steps contained water only. Fibre was squeezed in an SDL pad mangle (SDL Atlas Inc., England) after each step to remove excess liquor.

2.2.1.3 Ultrasonic bath
The ultrasonic bath used was a Decon FS300B (Decon Laboratories Ltd., United Kingdom). The unit has a working frequency of 40 kHz with frequency sweeping and a power level of 300 W. The bath dimensions were 300 mm wide, 320 mm long and 155 mm deep with a working volume of 11.0 l. Temperature control was achieved using a Thermoline L+M Unistat heater circulator (Thermoline Scientific Pty. Ltd., Australia) and the internal ultrasonic bath heater.

2.2.1.4 Mechanical agitation
Mechanical agitation was achieved using a Ratek OM6 Platform mixer (Ratek Instruments Pty. Ltd., Australia) set at 180 rpm.

2.2.1.5 Fibre diameter measurement
Mean fibre diameter was measured on the mechanically agitated scoured fibre using an OFDA2000 (BSC Electronics, Australia) according to AS/NZS 4492.5:2000 (Standards Australia/Standards New Zealand 2000b). Fibre samples were cut into 2 mm snippets and spread on a 70 mm square glass slide.
The whole slide was scanned with a minimum of four thousand fibres measured in each measurement. Five samples were measured for each test specimen.

2.2.1.6 Residual grease content
Residual grease content was measured using Soxhlet extraction according to the method given in Appendix C of the AS/NZS 4492.2:2000 (Standards Australia/Standards New Zealand 2000a). Three samples were measured for each of the scouring systems.

2.2.1.7 Colour measurement
Three 5.0 g wool samples from each scouring batch were arranged for colour measurement. The samples measured were over 5mm thick so that they were impermeable to light (HunterLab 2008). The fibres were arranged in a parallel aligned geometry to ensure a flat surface for fibre measurement and to avoid fibres entering the sphere. The samples were then measured using a Datacolor Spectraflash 600 spectrophotometer (Datacolor International, USA). Yellowness Index (YI) values were obtained using a standard illumination light D65.

2.2.1.8 Scouring loss
Scouring loss is the measure of mass lost from the greasy wool fibre during scouring represented as a percentage of the un-scoured mass and calculated using Equation 2.1

\[
SL\% = \left(\frac{Mg - Ms}{Mg}\right) \times 100
\]  

(2.1)

Where \( SL\% \) is the scouring loss in percent, \( Mg \) is the greasy mass of the wool fibre in grams and \( Ms \) is the scoured mass of the fibre in grams.
2.2.1.9 Fibre surface morphology
Fibre samples measured for surface morphology were first mounted on a 12.7 mm diameter aluminium electron microscope stub (Electron Microscopy Sciences, USA) using conductive tape (Ted Pella Inc., USA) before being gold sputter coated using an Emitech Polaron Q150T (Quorum Technologies Ltd., United Kingdom) to a coating thickness of 30-50 nm. The fibre surface before and after scouring was examined using a LEO1530 field emission gun scanning electron microscope (SEM). Measurements were conducted with an extra high tension voltage of 5 kV, a working distance of 15 cm and an aperture size of 60 μm.

2.2.2 Results and Discussion
2.2.2.1 Residual grease content
Figures 2.1, 2.2, 2.3 and 2.4 show the residual grease left in the wool after each of the scouring systems at the two scouring temperatures used. Figures 2.1 and 2.2 show the residual grease content after scouring at 60°C. The ultrasonically agitated 22 μm fibre had significantly lower residual grease content for the three lower detergent concentrations. This trend is also seen in the 18 μm fibre however the difference is not significant enough to substantiate the improvement.
**Figure 2.1** Residual grease content versus detergent concentration at 60ºC for 22 µm fibre

**Figure 2.2** Residual grease content versus detergent concentration at 60ºC for 18 µm fibre
As can be seen by comparing Figures 2.3 to 2.4 the reduction of scouring temperature affects the level of residual grease on the fibre scoured with mechanical agitation far more than that scoured with ultrasonic irradiation. The presence of cavitation events provided by ultrasonic irradiation assisted in the removal of grease and was more effective than mechanical agitation at the lower scouring temperature.
The residual grease content of wool fibre needs to be below 2% to make processing easier on the worsted spinning system (Bateup 1986). All of the ultrasonic irradiation scouring conditions used on the 22 μm wool at 50°C and 60°C produced fibres with a residual grease content below this figure. Most of the ultrasonically scoured 18 μm fibre at 60°C also had grease contents under 2%. The only sample with a grease content over 2% was the sample scoured with very low detergent concentration (0.05g/l). The same level of grease removal was not achieved for the 18 μm wool at 50°C as the starting grease content (17%) of the un-scoured fibre was almost double that of the 22 μm (9%) fibre and was harder to remove. The smaller the fibre diameter the larger the fibre surface area and fibre grease content is proportional to fibre surface area. This increase in grease content of the fibre means that it is significantly harder to scour hence the trial was conducted on wool of two mean fibre diameters.

2.2.2.2 Scouring loss
Scouring loss is a useful indicator of the effectiveness of a scouring method. As the level of contaminant removal increases, so does the loss during scouring. Figure 2.5 shows how the loss during scouring is greater for the 18 μm wool samples that have undergone ultrasonic irradiation for all of the detergent concentrations. This data mirrors the residual grease content data for the same scouring temperature.
2.2.2.3 Fibre yellowness

Fibre colour was not significantly affected by the scouring method. There was no significant difference in the colour of the fibre scoured with ultrasonic irradiation when compared with fibre scoured with mechanical agitation. An example of this is the YI value for 22 µm fibre scoured at 50°C. The ultrasonically agitated fibre has a YI of 17.21 and the mechanically agitated fibre has a YI of 17.35. These results are indicative of all of the other colour results. Changes in wool colour after scouring are generally affected by three mechanisms: alkali yellowing, temperature degradation and residual ash content. No significant change in yellowness index indicates that similar levels of dirt within the fibre are removed for ultrasonic irradiation to that of mechanical agitation. Similar yellowness index results also show that the sono-chemical effect of the ultrasonic irradiation does not accelerate alkali yellowing or temperature degradation.
2.2.2.4 Fibre entanglement
The level of fibre entanglement is an important factor in further processing and its effect on fibre length. The mechanically agitated fibres were moderately felted. The scoured fibre formed a mat that required force to tease apart. Samples that had undergone ultrasonic irradiation had minimal felting. The scoured fibre was easy to separate from the fibre bundle. The felting reduction in the ultrasonic samples could be attributed to the ultrasonically assisted liquor transfer not moving the fibres. Mass transfer in an environment subjected to ultrasonic irradiation, is by micro-streaming from bubble growth resonance and bubble collapse. The jet formed by a cavitation event next to a surface is projected at the surface at an angle perpendicular to the surface (Crum 1979). Displacement of the fibre would mostly occur in the direction of the cavitation jet which is perpendicular to the fibre. Fibre migration that leads to felting needs to occur in a direction parallel with the fibre. The dunking motion of mechanical agitation causes fibre displacement in all directions hence the number of fibre movements is higher and accordingly the fibre entanglement is higher. Fibre felting is quantified further in Section 2.3 of this Chapter.

2.2.2.5 Fibre surface changes
Figure 2.6 is an image of an un-scoured wool fibre and has been supplied for reference only. Figures 2.7 and 2.8 show the surface structure of individual wool fibres after scouring at 60°C with mechanical agitation and ultrasonic irradiation. The mechanical agitation scouring system produced the fibre shown in Figure 2.7. This is typical for this method of scouring. The fibre has had the grease and other surface contaminant removed and shows good scale definition and a clean surface. The fibre shown in Figure 2.8 has undergone scouring with ultrasonic irradiation. The fibre has a high level of contaminant
removal however it has surface cracking not seen in the conventionally scoured fibre.

Figure 2.6 SEM image of a typical un-scoured wool fibre from the 18 µm wool fleece
Figure 2.7 SEM image of a mechanically agitated wool fibre during scouring from the 18 µm wool fleece

Figure 2.8 SEM image of an ultrasonically irradiated wool fibre during scouring from the 18 µm wool fleece with surface cracks highlighted
Localized energy release at the fibre/liquid interface is likely to be responsible for the surface cracking. Bubble collapse induced by cavitation produces intense local heating (≈5000°C) and high pressures (≈500 Atmospheres) for very short lifetimes (Suslick 1990). The energy is localised and could impact heavily on the cuticle of the fibre causing the cracking. This fibre surface cracking phenomenon is discussed further in Chapter Four.

2.2.3 Conclusions
Ultrasonic irradiation assists with grease removal and enables a reduction in the detergent and temperature required for scouring. Fibre colour is not significantly affected by ultrasonic irradiation during scouring. Ultrasonic irradiation of a wool fibre in scouring liquor can cause micro-cracking to occur on the fibre surface. Further work has been conducted on quantifying fibre surface cracking and is presented in Chapter Four.

2.3 Fibre Felting Quantification after Carding

2.3.1 Experimental
2.3.1.1 Materials and sample preparation
Fibre used in this work was Australian merino wool grown in the Western District of Victoria, Australia. Fibre specifications after blending were 19.5 µm, 0.3 % vegetable matter, and a scouring yield 64.5 %. Fleece was opened before scouring by a single pass through a 500 mm wide single drum Fearnaught opener (Houget Duesberg Bosson, France).

2.3.1.2 Ultrasonic bath
Ultrasonic irradiation was conducted using a KQ-300VDE 10 litre ultrasonic bath (Kunshan Ultrasonic Instrument Co. Ltd., China). The bath is able to be
set to irradiate at 45/80 kHz with optional frequency sweeping, however, a fixed 45 kHz frequency was used for these experiments. The bath dimensions were 240 mm wide, 300 mm long and 150 mm deep with a working volume of 10.0 l. Power was set at maximum for all experiments (300 W) and temperature was set as per Table 2.1. Frequency sweeping was turned off for all experiments.

2.3.1.3 Mechanical agitation

Mechanical agitation was based on an industry rake scour motion and was achieved by using a reciprocating dunker with a 100 mm stroke and 20 cycles per minute. Mechanical agitation was used for all control samples.

2.3.1.4 Scouring bath parameters

Liquor ratio \((LR)\) is the amount of fibre within a bath versus the amount of scouring liquor used in the bath expressed as a ratio (Equation 2.2).

\[
LR = \frac{M_F}{M_{SL}} : \frac{M_{SL}}{M_F}
\]  

(2.2)

Where \(M_F\) is mass of fibre being scoured in grams and \(M_{SL}\) is the mass of the scouring liquor in grams.

A range of scouring bath liquor ratios (1:40, 1:80, 1:120, 1:200, and 1:400) were used for each of the different irradiation methods. The change in liquor ratio was achieved by keeping the liquor volume constant and varying the fibre mass used. Liquor ratios are expressed as fibre mass per volume of liquid (g/l) and called fibre density in the figures and discussions of this chapter as the trend is clearer in graphical form. Liquor ratios of 1:40, 1:80, 1:120, 1:200 and 1:400 have been expressed as 25.0, 12.5, 8.3, 5 and 2.5 g/l, respectively. The fibre density \((FD)\) was calculated using Equation 2.3.

\[
FD = \frac{M_F}{V_{SL}}
\]  

(2.3)
Where $V_{SL}$ is the scouring liquor volume in litres.

Scouring was undertaken using a conventional 5-bath method. Hydropol TN450 (Nonyl Phenol Ethoxylate detergent, Huntsman Chemicals) was used as the detergent, and sodium carbonate (Sigma-Aldrich Co., USA) as the alkali. Wool samples were conditioned and weighed before addition to the first scouring bath. Details for each bath of the process are given in Table 2.1.

**Table 2.1 Wool scouring bath parameters**

<table>
<thead>
<tr>
<th>Bath No</th>
<th>Function</th>
<th>Liquor composition</th>
<th>Temperature</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>desuinting</td>
<td>Water</td>
<td>35°C</td>
<td>3 mins</td>
</tr>
<tr>
<td>2</td>
<td>scouring</td>
<td>0.5 g/l Hydropol TN450</td>
<td>55°C</td>
<td>3 mins</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.2 g/l sodium carbonate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>scouring</td>
<td>0.5 g/l Hydropol TN450</td>
<td>55°C</td>
<td>3 mins</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.2 g/l sodium carbonate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>rinsing</td>
<td>Water</td>
<td>55°C</td>
<td>3 mins</td>
</tr>
<tr>
<td>5</td>
<td>rinsing</td>
<td>Water</td>
<td>55°C</td>
<td>3 mins</td>
</tr>
</tbody>
</table>

Fibres were squeezed with a Rapid PA0 pad mangle (Rapid Labortex Co.LTD., Taiwan) after each bath to remove excess liquor. After padding the water retained in the fibre was approximately 43% w/w. After scouring, the samples were dried in a Binder FED (Binder, Germany) fan forced oven at 105°C for 1 hour before conditioning, bagging and labelling.

**2.3.1.5 Carding**

The fibre was conditioned at $20\pm2$ °C and $65\pm2$% humidity for 24 hours before carding. Carding was undertaken with one pass of a Mesdan 337A carding
machine (Mesdan, Italy). Carding was undertaken without the application of a carding lubricant. The carded web was collected as a sliver to enable measurement of fibre diameter and length. The card was cleaned by fettling with a metal comb between each fibre batch to reduce contamination.

2.3.1.6 Fibre diameter and length measurement
An OFDA4000 (BSC Electronics, Australia) was used to measure the fibre diameter and length in the carded sliver. The OFDA4000 measures both fibre diameter and fibre length of a beard of fibres drawn from a sliver (Brims 2002). Fibres were sampled and scanned at three different sections of each sliver and a minimum of 3000 fibres were scanned in each measurement. Mean fibre length and mean fibre diameter were recorded for each test. Tests were conducted on card slivers from both the mechanically agitated and ultrasonically irradiated scoured fibre. Five tests were conducted for each scouring method. The percentage mean fibre length loss was calculated using Equation 2.4

\[
\text{Mean fibre length loss} (\%) = 100 \times \frac{(L_b - L_a)}{L_b}
\]  

(2.4)

Where \(L_b\) is the mean fibre length before scouring, and \(L_a\) is the mean fibre length after scouring.

Fibre length before scouring was determined from carding sliver from carded greasy fibre.

2.3.2 Results and Discussion
2.3.2.1 Fibre length changes
The percentage change in mean fibre length after carding for each of the scouring methods and fibre densities in the scouring liquor are shown in Figure 2.9. The fibre scoured using ultrasonic irradiation alone has a lower percentage
of mean fibre length loss for all of the scouring fibre densities. As the fibre density within the scouring bath increases, the percentage mean fibre length loss of the wool increases. This is expected as the fibre density within the scouring bath is directly related to the level of fibre entanglement. Fibres packed closely together have more chance of entanglement as their close proximity enables easy migration with limited liquor movement. As the level of entanglement increases, the mean fibre length after carding decreases as the opening process of carding breaks fibres that are heavily entangled instead of straightening them.

Figure 2.9 Mean fibre length loss of wool scoured with ultrasonic irradiation and mechanical agitation, at various liquor ratios

As the fibre density was increased mean fibre length of the carded fibre decreased for both ultrasonically irradiated and mechanically agitated scouring systems. Some of the fibre felting that causes fibre length loss is from fibre movement within the scouring bath; however, some felting also occurs during the fibre wet handling stages. The wet handling stages include wetting of the
fibre during addition to each bath, fibre removal from the scouring bath, and during padding to remove excess scouring liquor.

Mean fibre length measured for both the ultrasonically scoured and traditionally scoured wool fibre was significantly less than what would be expected in commercial carding. This is possibly due to excessive fibre breakage caused by carding without a carding lubricant in a sample woollen system card. Future work should be conducted to verify these findings at an industrial level with a commercially available carding lubricant.

2.3.2.2 Fibre diameter changes
OFDA 4000 (Figure 2.10) diameter measurements after carding versus liquor ratio results confirm that fibres scoured with mechanical agitation undergo a significant reduction in fibre diameter for high fibre densities. Necking of the fibre during stretch to break can be one cause for this if a sample has undergone a high level of fibre breakage. A previous study has shown that the diameter of broken fibres subjected to the stretch-break process was finer than the diameter of untreated fibres. Fibre diameter at the break point was the finest and was more irregular than the original fibre (Kwak et al. 2007). Carding of wool fibre with a high level of entanglement causes increased fibre breakage. As discussed in Section 2.2.2.5 mechanical agitation increases the level of fibre entanglement. Better diameter and length results for ultrasonically assisted wool scouring indicate that there is reduced entanglement if the rake motion is replaced by ultrasonic irradiation.
Figure 2.10 OFDA4000 measured mean fibre diameter after carding versus scouring liquor ratio

2.3.3 Conclusions
Samples that had undergone ultrasonic irradiation during scouring appear to have had less fibre breakage during carding despite micro-cracking (Figure 2.8). Ultrasonic irradiation causes less movement of the fibres during scouring resulting in less fibre entanglement. Fibre diameter was unaffected by ultrasonic irradiation during scouring.

2.4 Ultrasonic Energy Transfer within the Scouring Bath

2.4.1 Experimental
2.4.1.1 Materials
Aluminium foil used in these experiments was 30 µm thick OSO all-purpose aluminium foil (Clorox Australia Pty. Ltd., Australia). Fibre used was from a single, blended un-scoured Australian merino fleece sourced from the Western district of Victoria, Australia. The fleece had a mean fibre diameter of 21.3 µm and coefficient of variation in fibre diameter of 23.2%.
2.4.1.2 Foil placement
Aluminium foil was cut into squares 60 x 60 mm in size and mounted in a steel sample holder. The sample holder was made from 1.40 mm thick steel and had external dimensions of 60 x 60 mm and an internal window of 30 x 30 mm where the aluminium foil was exposed. Samples were ultrasonically irradiated for 60 seconds, at constant positions, both horizontally (Figure 2.11) and vertically (Figure 2.12).

![Figure 2.11](image)

Figure 2.11 Horizontal foil orientation side view and top view respectively

![Figure 2.12](image)

Figure 2.12 Vertical foil orientation side view and top view respectively

2.4.1.3 Processing conditions
The ultrasonic bath was filled with 10.0 l of water with 0.5 g/l Hydropol TN450 and 0.2 g/l sodium carbonate. The ultrasonic bath was heated to 60°C and the bath was run for 60 minutes to ensure complete degassing of the
treatment liquor. Unprocessed wool fibre was added to the ultrasonic bath with a starting mass of 5.0±0.05 g. The mass of wool was increased at 5.0 g increments until foil damage was minimised. After each addition of wool fibre to the bath 15 minutes of degassing was undertaken before a new sample of aluminium was inserted.

2.4.1.4 Ultrasonic bath
The ultrasonic bath used was the same as that detailed in Section 2.2.1.3.

2.4.1.5 Image analysis
Photographs of the samples were taken and manipulated using GNU Image Manipulation Program (GIMP, www.gimp.org) to allow the area of any holes or indentations to be quantified. Image J (Abramoff et al. 2004) was used to determine the boundaries of any distortions in the aluminium sheet. Foil damage was measured in terms of the total area of the holes or distortions caused by the cavitation implosions.

2.4.2 Results and Discussion
Figure 2.13 shows the area of ultrasonic erosion seen in the aluminium foil for each of the scouring fibre densities investigated. The scale is shown in mass per volume (g/l) of fibre with reference to liquor volume. As the bath was held at 11.0 l for all experiments 5.0, 10.0, 15.0 and 20.0 g of fibre added corresponds to 0.45, 0.90, 1.35 and 1.80 g/l, respectively. Wool is an effective absorber of ultrasound. The trend observed in Figure 2.13 shows that ultrasonic intensity was dramatically reduced when wool fibre was present. Little or no damage was seen after 20.0 g of fibre had been added. When foil was irradiated in a horizontal orientation slightly greater damage was seen. This is consistent with the high levels of absorption making the direct sound path more important.
During processing there was a high level of inconsistency in the results, which may have been caused by inadequate de-gassing and uneven fibre distribution within the bath. Movement of fibre around the bath from ultrasonically induced local water flow would result in changes of local ultrasonic intensity.

**Figure 2.13** Area eroded as a function of wool fibre mass per unit volume

Figure 2.14 (a) shows a piece of foil from the horizontal plane which has undergone a high level of erosion during irradiation. There are two types of cavitation effects seen on the foil; indentation and erosion. Both were measured for this study and summed to provide the total cavitation area. Figure 2.14 (b) shows the foil after image manipulation. Image manipulation was undertaken to enable accurate indent and erosion (cavitation) area estimation. Figure 2.15 (a) shows a piece of foil that has undergone irradiation in the vertical plane with its subsequent manipulated image (Figure 2.15(b)).
Figure 2.14 Foil image (0.45g/l horizontal plane) showing large scale erosion from ultrasonic cavitation – before (a) and after (b) image manipulation

Figure 2.15 Foil image (0.45g/l, vertical plane) showing low levels of erosion from ultrasonic cavitation – before (a) and after (b) image manipulation

2.4.3 Conclusions
Wool present in an ultrasonic scouring bath absorbs ultrasonic irradiation. Absorption increased with increasing wool fibre mass with no erosion of 30µm aluminium foil seen after a fibre density of 1.80 g/l was reached.
2.5 Effect of Fibre Loading on Cleaning Efficiency

2.5.1 Experimental
The materials and sample preparation, scouring equipment and scouring bath parameters were the same as those reported in Sections 2.3.1.1, 2.3.1.2, 2.3.1.3 and 2.3.1.4 of this Chapter.

2.5.1.1 Residual ash content, residual grease content and fibre whiteness
Each sample of scoured fibre was placed randomly in a plastic petri dish. Three samples from each scouring method were measured in a Near Infrared Spectroscopy (NIR) system by the Australian Wool Testing Authority (Melbourne, Australia) for grease content, ash content, and fibre whiteness, according to AS/NZS 4492.2:2000 (Standards Australia/Standards New Zealand 2000a). The grease content was measured using Soxhlet extraction and ash content using the thimble burn method, both according to AS/NZS 4492.2:2000 (Standards Australia/Standards New Zealand 2000a), to confirm calibration of the NIR.

2.5.2 Results and Discussion
In the previous Section of this Chapter it was noted that there was very little erosion of aluminium foil within the bath when the fibre density was greater than 1.8 g/l. The results presented in Figure 2.16 suggest that the benefits of ultrasonic irradiation for scouring performance were maintained up to a fibre density of 8.3 g/l (liquor ratio of 120:1). Above this fibre density each of the parameters of residual grease content, residual ash content and fibre brightness deteriorated with increasing fibre density. The results of the previous Section of this Chapter suggested the significantly reduced cavitation for fibre densities above 1.8 g/l would mean that ultrasonic wool scouring would not be effective. These results suggest that cavitation damage to 30 µm aluminium foil may not...
be sensitive enough to be an indicator for energy transfer within a wool scouring bath. The level of wetting within the bath may also have contributed to the improvement in transmission of ultrasonic irradiation within the bath (Datar et al. 1996b). The padding and rewetting step between each bath could help displace trapped air within the fibre. Each successive bath would have better transmission than the first as the level of wetting is increased. Air provided to the system of each bath, after the first, would be decreased as the pre-wet fibre would not have as much air trapped within its internal structure. An increase in air within the bath reduces the ultrasonic intensity within a bath due to cushioning of the cavitation event.

![Graph](image)

**Figure 2.16** Residual ash content, residual grease content and whiteness of wool scoured with ultrasonic irradiation at various liquor ratios

### 2.5.3 Conclusion

Low levels of ultrasonic irradiation are still effective in producing adequate wool scouring. Wool density did not start to impact on scouring efficiency, for
the wool and scouring conditions tested, until a wool fibre density of over 8.3 g/l was reached.

### 2.6 Chapter Summary

The use of ultrasonic irradiation instead of a rake scouring action during wool scouring assists with grease removal and enables a reduction in the detergent and temperature required for scouring. Ultrasonic irradiation causes less movement of the fibres than the rake action resulting in less fibre entanglement. Less fibre entanglement is confirmed by less fibre breakage or diameter change during subsequent carding.

Fibre colour is not significantly affected by ultrasonic irradiation during scouring. Micro-cracking of the fibre cuticle is observed in samples that have been ultrasonically irradiated during scouring. Further work has been conducted on quantifying fibre surface cracking and is presented in Chapter Four.

Wool present in an ultrasonic scouring bath absorbs ultrasonic irradiation. Absorption increased with increasing wool fibre with no erosion of 30µm aluminium foil seen above a fibre density of 1.8 g/l. Adsorption trials utilising grease removal, colour and ash content as the indicators showed that wool density does not start to impact on scouring efficiency until a wool fibre density of above 8.3 g/l is reached. High levels of ultrasonic irradiation adsorption caused by high fibre density are still effective in producing adequate wool scouring.
3 Ultrasonic Laundering of Fabrics

3.1 Introduction

A textile garment will require cleaning during its lifetime. It is important to maintain garment appearance and properties after the cleaning process. Damage to a wool garment during cleaning is a common occurrence due to incorrect cleaning methods used by consumers. There are a number of conventional and non-conventional ways of cleaning fabrics. The two most accepted systems are aqueous laundering and dry cleaning. Hand washing and machine washing are the standard methods for aqueous laundering with the method dictated by the fibre type, fabric construction and garment intricacy. Selecting the correct detergent system is also important and is fibre dependant.

The main factors that cause damage to a wool garment during cleaning are felting shrinkage, detergent selection and laundering temperature. Laundering temperature and detergent selection are easily controlled by the person doing the laundering, however, washing machine design is not. The main contributing factor to felting shrinkage during laundering is excessive movement of the item being cleaned while in a wet state.

Fabric felting is an irreversible entanglement of the wool fibre. Felting within a fabric causes dimensional shrinkage and thickness increase, which affect garment size and appearance. The movement of wool fibres within a fabric, especially in a wet environment, can easily occur in one direction along the fibre but not in the other due to the cuticle structure of wool. A garment in a cleaning vessel (hand or machine agitated) moves around with the protruding
fabric edges impacting the sides of the vessel. Fibres within the outer edge of the fabric move towards the centre away from the impact and ratchet together due to the scale structure. This fibre movement within the fabric structure causes dimensional shrinkage and fabric consolidation.

The normal method adopted for liquor movement and particle detachment during laundering is movement of the fabric within the wash bath. This is achieved during hand washing by stirring or dunking of the fabric within the cleaning liquor. This is achieved in a top loading washing machine by moving the wash liquor and fabric with a paddle agitator. This is achieved in a front-loading washing machine by rotating the fabrics within a drum-like mesh basket within the wash liquor. Washing machine design is based around an agitator or drum moving the fabric through a liquid. These machines are relatively easy to build, robust and provide good cleaning liquor transfer through the item being cleaned. A static cleaning bath would provide less damage to garments, however cleaning would be reduced due to decreased liquor transfer through the fabric and so this method is not used apart from when cleaning very delicate fabrics.

Ultrasonic irradiation could be used to provide liquor movement and particle detachment in a static environment without reducing cleaning efficiency. Bubble implosions and micro-streaming within the cleaning liquor provide fluid movement, while bubble implosions close to a surface provide high speed liquid jets for physical detachment. All of this is achieved with little or no fabric or fibre movement, or the subsequent abrasion or pilling that is experienced in fabric movement style washing environments.
Ultrasonic irradiation is not new to the textile industry (Effect of Ultrasonic Energy on Fibrous Materials 1954; Goodman and Hilton 1963). Initial investigations date back to 1954. New technologies are required to reduce the cost and environmental impact of textile processing, so researchers have again looked at the use of ultrasonic agitation to provide unique mass transfer (Moholkar and Warmoeskerken 2004) within the processing liquor. Recent investigations include dyeing (Shimizu et al. 1989), bleaching (Mistik and Yukseloglu 2005), bast fibre degumming (Hurren et al. 2004; Wang and Wang 2004; Fakin et al. 2005), fabric softening (Parvinzadeh et al. 2010) and enzyme desizing (Yachmenev et al. 2002). There has been some interest in ultrasonic cleaning of different fabrics (Canoglu et al. 2004; Vouters et al. 2004), but little has been reported on how ultrasonics affect the properties of wool fabrics.

Investigations into the use of ultrasonic irradiation in the domestic laundering of wool are reported in this Chapter. A number of factors have been investigated that relate directly to fabric quality and appearance after laundering. Four separate experiments are presented each with its own experimental conditions, results, discussion and conclusions. The overall findings are summarised at the end of the chapter.

The first experiment examines the effect of ultrasonic irradiation during wool fabric washing on fabric dimensional stability. The second experiment quantifies the effectiveness of ultrasonic irradiation in a stationary laundering bath on the removal of the common stains black tea, black coffee, red wine, orange carbonated soft drink and engine oil. The third experiment looks at the effect of ultrasonic irradiation during fabric laundering on Martindale abrasion resistance of woven fabrics without a shrink-proof finish. The fourth
experiment examines the effect of ultrasonic irradiation during fabric laundering on pilling propensity.

3.2 Dimensional Changes

3.2.1 Experimental

3.2.1.1 Fabric specifications and preparation
Greige fabric samples used were from a 240 g.m\(^{-2}\) 100% wool broken-twill fabric. The fabric was constructed with 37 two-ply ends.cm\(^{-1}\) in the warp and 33 single-ply picks.cm\(^{-1}\) in the weft. The fabric was scoured in 200 mm warp length pieces by the full fabric width in the weft direction before experiments were conducted. Scouring was undertaken in a solution of 1.0 g/l Solpon 2448 (Boehme Group, Germany) and 0.5 g/l of sodium carbonate (Sigma-Aldrich Co., USA) at 60\(^{\circ}\)C for 20 min using a liquor ratio of 10:1. The fabrics were then padded to a liquor content of 80% in a Rapid PA0 pad mangle (Rapid Labortex Co. Ltd., Taiwan) before being rinsed in warm water twice, with padding after each rinse. After the final padding they were dried at 105\(^{\circ}\)C flat and without tension in a laboratory oven for one hour before being conditioned according to AS2001.1 1995 (Standards Australia 1995). After conditioning the test fabrics were measured for dimensional size, colour, thickness, tensile properties and visual appearance.

3.2.1.2 Dimensional stability measurement
The fabrics were marked up for assessment of dimensional stability by sewing a thread into each corner of two 150 mm x 150 mm squares centred on the right hand end of the fabric. The sides of each square were measured for length and the results recorded. The marking system and pattern for measuring each square is shown in Figure 3.1.
Figure 3.1 Marking and measurement pattern for fabric dimensional stability

Mean percentage width, length and area dimensional changes were calculated according to Equations 3.1, 3.2 and 3.3, respectively.

\[
\Delta W^\% = \left[ \frac{(W_{1b} - W_{1a})}{W_{1b}} + \frac{(W_{2b} - W_{2a})}{W_{2b}} + \frac{(W_{3b} - W_{3a})}{W_{3b}} + \frac{(W_{4b} - W_{4a})}{W_{4b}} \right] \times 100 \frac{1}{4}
\]

(3.1)

where \(\Delta W^\%\) is the percentage width dimensional change, \(b\) denotes dimension measurements taken before treatment, \(a\) denotes dimension measurements taken after treatment and \(W_1, W_2, W_3\) and \(W_4\) are described in Figure 3.1.

\[
\Delta L^\% = \left[ \frac{(L_{1b} - L_{1a})}{L_{1b}} + \frac{(L_{2b} - L_{2a})}{L_{2b}} + \frac{(L_{3b} - L_{3a})}{L_{3b}} + \frac{(L_{4b} - L_{4a})}{L_{4b}} \right] \times 100 \frac{1}{4}
\]

(3.2)

where \(\Delta L^\%\) is the percentage length dimensional change and \(L_1, L_2, L_3\) and \(L_4\) are described in Figure 3.1.

\[
\Delta A^\% = \Delta L^\% + \Delta W^\% - \left( \frac{\Delta L^\% \times \Delta W^\%}{100} \right)
\]

(3.3)

where \(\Delta A^\%\) is the percentage area dimensional change.
3.2.1.3 Colour measurement
Fabrics were measured for CIE L*, a*, b* colour space values using a Datacolor Spectraflash 600 (Datacolor International, USA). Measurements were taken using the standard illuminant D65 and a LAV aperture with specular included and 10° field of view width. Four measurement cycles with five spectral captures per cycle were conducted for each sample.

3.2.1.4 Fabric thickness measurement
Fabric thickness was measured using a Mesdan LAB digital thickness tester (Mesdan S. p. A., Italy) at a shoe pressure of 0.5 kPa. Each fabric was measured ten times and the mean value calculated.

3.2.1.5 Fabric tensile properties
Tensile property measurements were conducted in a strip test format according to AS2001.2.3.1 (Standards Australia 2001) using a Lloyd LR30K tensile tester (Lloyd Instruments, United Kingdom). A gauge length of 100 mm and test width of 50 mm were used. Fabrics strips were prepared 60mm wide and an even edge was frayed on each side to provide a test sample that was 50mm wide. A rate of extension of 100 mm/min was used for all tests. Ten tensile samples were tested for each fabric laundering system and the mean reported.

3.2.1.6 Ultrasonic bath
The ultrasonic bath used in this experiment is the same as that detailed in Chapter Two Section 2.2.1.3.

3.2.1.7 Ultrasonic washing method
Each of the ultrasonic treatments was carried out at a liquor ratio of 100:1. The bath working frequency was 35-45 kHz (sweeping). All experiments were carried out at 60°C. The liquor was degassed using 60 minutes of ultrasonic irradiation before each experiment was conducted. Fabric samples were placed
directly into the wash liquor contained within the bath and were free to move within the bath.

The dimensional stability experiments involved repeated wash/dry cycles using ultrasonic irradiation in comparison with hand agitation. The two samples (hand agitation and ultrasonic irradiation) were run in tandem through a series of ten, 60 minute wash and dry cycles. The liquor used contained 0.5 g/l Hydropol TN450 (Huntsman International LLC., USA) and 0.2 g/l sodium carbonate (Sigma-Aldrich Co., USA).

After each of the treatments, the fabric was hand rinsed three times in water with a temperature of 50°C. After rinsing, each of the samples was padded to 80% liquor content in a Rapid PA0 Pad mangle to remove excess water before being oven dried at 105°C for one hour.

3.2.1.8 Measurements during and after treatment
Colour and dimensional change measurements were made after every wash. Fabric thickness was measured after every second wash. Tensile properties were measured at the completion of the tenth wash/dry cycle. Before measurement the fabric samples were conditioned according to AS2001.1 1995 (Standards Australia 1995).

3.2.1.9 Fibre surface morphology
The electron microscopy methods used to examine fibre surface morphology are the same as those given in Chapter Two Section 2.2.1.9

3.2.2 Results and Discussion
3.2.2.1 Fabric thickness and dimensional stability
Figure 3.2 shows that there is a small but significant difference in fabric thickness between the two washing methods. The fabrics that had undergone
ultrasonic irradiation during laundering did not increase in thickness as quickly as the fabric that had undergone hand washing. The progressive increase in thickness of wool fabrics during laundering is linked to felting shrinkage. After the initial big reduction in the fabric dimensions in the first two cycles of the laundering process, there is a steady decrease in dimensions with each successive wash cycle (Figure 3.3). The dimensional shrinkage is smaller for the fabric that has undergone ultrasonic irradiation rather than hand agitation. The steady decrease in fabric dimensions are consistent with the steady increase in thickness and confirm that felting shrinkage is occurring.

The liquor transfer in the hand agitated washing was provided by stirring and plunging the fabric at intervals throughout the wash cycle. The ultrasonic irradiation did not have this mechanical stirring or plunging, its liquor transfer relied on the ultrasonic cavitation implosions within the bath and at the liquid/solid interface of the fibre. The ultrasonic irradiation did not produce the fibre migration seen with the hand agitated fabric, and this reduced the felting, dimensional shrinkage and thickness increase while maintaining liquid mass transfer.
Figure 3.2 Change in fabric thickness with repeated washing

Figure 3.3 Fabric area dimensional shrinkage with repeated washing
3.2.2.2 Colour
Washing causes a change in the fabric colour. As each sequential wash occurs the temperature degradation during washing and drying combined with alkali damage causes fabric yellowing. This is observed as a shift of colour in the red (increase in a*) and yellow (increase in b*) directions of the CIE L*, a*, b* colour space (Figure 3.4). Yellowing is also exhibited as an increase of depth of colour (decrease in L*). Ultrasonic irradiation had the same influence on fabric colour during laundering as hand agitation did. An increased yellowing of an undyed fabric during ultrasonic irradiation when compared with hand agitation would be undesirable as it could show a modification of the fibre not seen with mechanical agitation.

3.2.2.3 Fibre surface morphology
Micro-cracking of the fibre surface was observed in fabric samples that had undergone ultrasonic irradiation. Micro-cracking was only evident in samples that had undergone ultrasonic irradiation and were similar in morphology to those observed in Chapter Two Section 2.2.2.5. This fibre surface cracking phenomenon is discussed further in Chapter Four.

3.2.2.4 Fabric tensile properties
Significant damage to fibre structure by ultrasonic irradiation should adversely affect the tensile properties of the fibre. However, after ten washing cycles there was no significant difference between the tensile properties. The results showed a mean breaking force of 348.4 N for the ultrasonic irradiated fabric and 348.0 N for the hand washed fabric. The percentage strain to break was the same (83.0%) for each laundering method.
3.2.3 Conclusions
Ultrasonic irradiation during laundering of wool fabrics in a static bath, instead of hand washing, leads to less felting and a smaller increase in fabric thickness however the level of felting is still at undesirable levels. Ultrasonic laundering can cause micro-cracks to form in the scale structure of the wool fibre but these cracks have a negligible impact on fabric strength. When compared with hand agitation, ultrasonic laundering has negligible difference in the effect on the colour of an undyed wool fabric during a repeated wash dry cycle.

Figure 3.4 Change in fabric colour (L*, a* and b* values) with repeated washing
3.3 Stain Removal

3.3.1 Experimental
3.3.1.1 Fabric specifications and preparation
The fabric used, and fabric preparation method was the same as that detailed in Section 3.2.1.1

3.3.1.2 Stain preparation
Five common stains: coffee, tea, red wine, engine oil and orange carbonated drink were investigated. The coffee stain was produced by placing 5.0 g of Maccona® Classic Medium Roast instant coffee powder (Douwe Egberts, Netherlands) into 250 ml of boiling deionised water. The tea stain was produced by placing one Lipton Quality Black Tea tea-bag (Unilever, United Kingdom) into 250 ml of boiling deionised water. The red wine stain was 2002 vintage Waurn Ponds Estate Shiraz (Waurn Ponds Estate, Australia), the orange carbonated drink stain was Fanta (The Coca Cola Company, USA) and engine oil stain was Castrol GTX3 SAE 5-40 grade engine oil (Castrol Limited, United Kingdom). All were applied to the fabric in an undiluted form.

3.3.1.3 Staining method
A piece of the test fabric was thoroughly wet out in a bath of the stain over a 24 hour period. The starting temperature of the coffee and tea was 95°C. The starting temperature of the red wine, Fanta and oil was 20°C. The fabric was then padded to a pick-up of 85% for all of the stains, with the exception of the oil which was 110%, before being dried for one hour at 105°C.

3.3.1.4 Laundering
The stained fabric was measured for colour change from unstained before being cut into 200 mm x 200 mm squares. Two stained fabric samples were then washed in tandem for 30 minutes using ultrasonic irradiation or hand agitation. Two wash liquors were used. One contained 0.5 g/l Hydropol TN450
(Huntsman International LLC., USA) and 0.2 g/l sodium carbonate (Sigma-Aldrich Co., USA) and the other contained 1.0 g/l Softly™ (A buffered pH wool detergent, Pental Products Pty, Australia). After each of the treatments, the fabric was hand rinsed three times in water at 50°C. After rinsing, each of the samples was padded to 80% water content to remove excess water before being oven dried at 105°C for one hour. The fabric samples were then conditioned for a minimum of 24 hours at 20±2 °C and 65±2 % humidity before being measured for colour change.

3.3.1.5 Ultrasonic bath
The bath used for this experiment is the same as that detailed in Chapter Two, Section 2.2.1.3. All experiments were carried out at a liquor ratio of 100:1 and at a temperature of 60°C.

3.3.1.6 Colour measurement
All colour measurements were undertaken using the same method described in Section 3.2.1.3

3.3.2 Results and Discussion
Figures 3.5 and 3.6 show the results of laundering trials after hot and cold staining. The change in shade after laundering was greater, i.e. more stain was removed, for the ultrasonically irradiated fabrics for both detergent systems. The Softly™ wool wash detergent did not always give the significant difference seen with the Hydropol TN450, but this was stain type dependent. A difference between the two detergents is expected as the Hydropol TN450 experiments were carried out under alkaline conditions, whereas the Softly experiments were carried out at a neutral to slightly acidic pH. Results of trials conducted using oil as the stain were similar to those reported for the other stains with the ultrasonically irradiated fabric ΔE of 3.49 for Softly™ and 1.18
for Hydropol TN450, and the hand wash $\Delta E$ of 0.37 for Softly™ and 1.12 for Hydropol TN450.

**Figure 3.5** Change in shade after laundering for hot stains

**Figure 3.6** Change in shade after laundering for cold stains

The improvement in stain removal by ultrasonic irradiation can be explained by several factors. Ultrasonic irradiation provides a higher velocity of the laundering solution at the fibre surface. This increased velocity improves the mechanical removal of the stain from the surface of the fibre. The increase in
velocity is achieved by the ultrasonic irradiation providing a decrease in the stationary liquor boundary layer thickness next to the fibre. A large boundary layer restricts cleaning chemistry interaction with the contaminant. A reduction in the boundary layer enables the micro-jets, from close to surface cavitation events, to impact directly on the contaminant enabling breaking of bonding forces (McQueen 1986; Fuchs 2001).

Stain dissolution within the laundering solution is improved as cavitation events reduce the size of agglomerated stains and aid in micelle encapsulation. A well encapsulated small stain does not easily redeposit onto the cleaned surface due to steric hindrance for non-ionic surfactants (Awad 2001).

High mass transfer rates within the ultrasonically irradiated liquor enable removal of stoichiometrically exhausted cleaning liquor from the surface of the fibre and from within the fabric structure. The exhausted liquor is replaced with less exhausted liquor that continues contaminant removal. Without effective removal of this liquor the rate of cleaning would reduce or stall. The mass transfer improvements offered by ultrasonics ensure that liquor transfer is high even within the complicated fabric structure (Moholkar and Warmoeskerken 2004; Moholkar et al. 2004).

### 3.3.3 Conclusions

The ultrasonic irradiation conditions used here in a static bath laundering of wool fabric provided better stain removal for the same detergent concentration and laundering temperature than hand washing while reducing the felting shrinkage. It is suggested that the improvement in cleaning is provided by improved stain dissolution, improved mass transfer and a reduced boundary layer.
3.4 Fabric Abrasion and Pilling

3.4.1 Experimental

3.4.1.1 Fabric specifications and preparation
The fabric used, and fabric preparation method were the same as that detailed in Section 3.2.1.1

3.4.1.2 Ultrasonic treatment
The ultrasonic bath used for this experiment is the same as that detailed in Chapter Two Section 2.2.1.3. All experiments were carried out at a liquor ratio of 100:1 and at a temperature of 60°C. Treatment time was 90 minutes and the liquor contents of each treatment bath are given in Table 3.1. The fabric was left static in each bath without agitation or stirring. Three different pH conditions were used for the experiments to simulate laundering under alkaline, neutral and acidic conditions. A control bath was used for each of the different pH conditions as fibre abrasion properties could be changed by the treatment liquor pH. The control bath was identical to the ultrasonic treatment bath (time, temperature, liquor ratio, and chemical composition) without the ultrasonic irradiation.

**Table 3.1** Treatment liquor conditions

<table>
<thead>
<tr>
<th>Method number</th>
<th>Treatment liquor composition</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkaline Ultrasonic (1)</td>
<td>0.5 g/l Hydropol TN450</td>
<td>8.62</td>
</tr>
<tr>
<td></td>
<td>0.2 g/l Sodium carbonate (Na₂CO₃)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.1 g/l Ammonium sulphate</td>
<td></td>
</tr>
<tr>
<td>Alkaline Control</td>
<td>0.5 g/l Hydropol TN450</td>
<td>8.79</td>
</tr>
</tbody>
</table>
(2) 0.2 g/l Sodium carbonate (Na$_2$CO$_3$)  
0.1 g/l Ammonium sulphate  

Neutral Ultrasonic  
0.5 g/l Hydropol TN450 7.01  
(3) 0.6 g/l Ammonium sulphate  

Neutral Control  
0.5 g/l Hydropol TN450 7.07  
(4) 0.6 g/l Ammonium sulphate  

Acidic Ultrasonic  
0.5 g/l Hydropol TN450 4.41  
(5) 0.2 g/l Acetic Acid  

Acidic Control  
0.5 g/l Hydropol TN450 4.31  
(6) 0.2 g/l Acetic acid  

After treatment the fabric was hand rinsed three times in 50°C water. After rinsing, each of the samples was padded to 80% liquor content in a Rapid PA0 Pad mangle to remove excess water before being oven dried at 105°C for one hour. Dried fabrics were allowed to condition for a minimum of 24 hours at 20±2 ºC and 65±2 % humidity before Martindale abrasion testing.

**3.4.1.3 Martindale abrasion testing**

Testing was undertaken in a Martindale abrasion tester (IDM Instruments, Australia). Fabrics were assessed for weight loss and appearance change from Martindale abrasion according to AS2001.2.25.3-2006 (Standards Australia 2006a) and AS2001.2.25.4-2006 (Standards Australia 2006b) respectively. The laundered fabric was placed over the top of a 140 mm diameter non-woven felt
disk (SDL Atlas, United Kingdom) and tightened in place in the fixed position mounting station. An SM25 abradant fabric (SDL Atlas, United Kingdom) was placed into the 38 mm diameter oscillating test head. Testing was undertaken at 9.0 kPa of pressure and samples were tested for mass loss after the 1 000, 2 500, 5 000, 7 500 and 10 000th cycle.

Appearance change was assessed by comparing the samples after 10 000 cycles using a Pillgrade automated pilling assessment unit (Line Tech Industries Inc, America). The four samples that had been subjected to Martindale abrasion were cut into 90 mm length by 90 mm width squares. The cut samples were passed through the Pillgrade unit making sure that the warp direction of the fabric was parallel with the machine feed direction. The pilling rating was averaged for each of the measurements with the mean and standard deviation reported.

3.4.2 Results and Discussion
Figures 3.7, 3.8 and 3.9 contain the results of the percentage mass change in the laundered fabrics during and after Martindale abrasion testing. There is no discernible difference between the control and the ultrasonically treated fabrics within the pH group or across the pH groups. These fabrics were processed at the same time and in the same treatment liquor as the samples presented in Chapter Four, Section 4.3 and 4.4. Electron microscopy of fibres present in the fibre bath show that fibre cuticle cracking was present in this experiment. Images of the type of cracking present in the fibre samples have been shown in Chapter Four, Figures 4.16, 4.17 and 4.18. The rate of mass loss is typical for a woven wool fabric undergoing Martindale abrasion with an initial rapid weight loss followed by a plateau. The results are similar for the pilling ratings given
in Table 3.2. After abrasion all of the fabrics exhibited slight fuzzing on their surface. The results indicate that the cuticle surface changes observed after exposure to ultrasonic irradiation in an aqueous environment have negligible impact on Martindale abrasion resistance.

![Figure 3.7 Weight loss during Martindale abrasion for alkaline pH laundered fabric](image)

**Figure 3.7** Weight loss during Martindale abrasion for alkaline pH laundered fabric
Figure 3.8 Weight loss during Martindale abrasion for neutral pH laundered fabric

Figure 3.9 Weight loss during Martindale abrasion for acidic pH laundered fabric
### Table 3.2 Martindale abrasion appearance rating results

<table>
<thead>
<tr>
<th>Method number</th>
<th>Mean Rating</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkaline Ultrasonic</td>
<td>1.9</td>
<td>0.33</td>
</tr>
<tr>
<td>Alkaline Control</td>
<td>2.8</td>
<td>0.70</td>
</tr>
<tr>
<td>Neutral Ultrasonic</td>
<td>2.3</td>
<td>0.21</td>
</tr>
<tr>
<td>Neutral Control</td>
<td>3.4</td>
<td>0.13</td>
</tr>
<tr>
<td>Acidic Ultrasonic</td>
<td>2.4</td>
<td>0.25</td>
</tr>
<tr>
<td>Acidic Control</td>
<td>1.9</td>
<td>0.19</td>
</tr>
</tbody>
</table>

#### 3.4.3 Conclusions
The ultrasonic irradiation of a woven wool fabric has negligible effect on its resistance to Martindale abrasion with no discernible difference in mass loss or surface appearance change when compared with hand washing.
3.5 Fabric Pilling

3.5.1 Experimental

3.5.1.1 Fabric specifications and preparation
Two knitted fabrics were used for the pilling trials. All fabrics were 100% wool. The first knitted fabric was a 316 g/m² single jersey. It was knitted on a 36 gauge Mesdan Lab Knitter 294E (Mesdan S. p. A., Italy) from 3 ends of 20 tex singles wool yarn. The second knitted fabric was a 233 g/m² Only Ewe™ Australian fine merino interlock superwash wool fabric (Only Ewe Textiles International, Australia). The yarn had been treated with a chlorine/Hercosett shrink resist treatment before knitting to provide a machine wash level of shrink resistance. The fabric was a proprietary product and exact details of the shrink resist process are not known. The fabric preparation method for both fabrics was the same as that detailed in Section 3.2.1.1

3.5.1.2 Ultrasonic treatment
The ultrasonic and control treatment method was the same as that detailed in Section 3.4.1.2.

3.5.1.3 Pilling testing and assessment
Pilling testing was conducted in an Orbitor two station ICI style pill box (James H Heal and Co Ltd, England) with cork lining material. Testing was conducted according to ISO standard 12945-1:2000 (International Standards Organisation 2000). All samples were subjected to 14,400 revolutions.

Change in appearance was assessed by comparing the samples after 10,000 cycles using a Pillgrade automated pilling assessment unit (Line Tech Industries Inc, America). The four samples that had been subjected to pilling assessment were cut into 90 mm length by 90 mm width squares. The cut samples were passed through the Pillgrade unit making sure that the warp
direction of the fabric was parallel with the machine feed direction. The rating was averaged for each of the measurements with the mean and standard deviation reported.

### 3.5.2 Results and Discussion

**Table 3.3** ICI pilling appearance rating results

<table>
<thead>
<tr>
<th>Method number</th>
<th>Jersey</th>
<th>Interlock</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkaline Ultrasonic</td>
<td>3.6 (0.71)</td>
<td>4.8 (0.2)</td>
</tr>
<tr>
<td>Alkaline Control</td>
<td>4.0 (0.43)</td>
<td>4.8 (0.2)</td>
</tr>
<tr>
<td>Neutral Ultrasonic</td>
<td>3.8 (0.47)</td>
<td>4.7 (0.19)</td>
</tr>
<tr>
<td>Neutral Control</td>
<td>4.4 (0.48)</td>
<td>4.9 (0.22)</td>
</tr>
<tr>
<td>Acidic Ultrasonic</td>
<td>4.1 (0.15)</td>
<td>4.7 (0.29)</td>
</tr>
<tr>
<td>Acidic Control</td>
<td>3.9 (0.48)</td>
<td>5.0 (0.09)</td>
</tr>
</tbody>
</table>

Table 3.3 shows the ratings for the ICI pilling tests. As observed with the Martindale abrasion results, there was no significant visual or measured difference between the pilling samples. Each of the surfaces had undergone a
light fuzzing with the appearance of a small number of pills (5-20 single jersey and 0-5 interlock). None of the different treatment pHs showed a different trend. The trend was the same for the single jersey and the interlock fabrics.

Table 3.03 ICI pilling appearance rating results

3.5.3 Conclusions
Ultrasonic irradiation of a knitted wool fabric has a negligible effect on its propensity for pilling on both untreated and chlorine/Hercosett treated wools. There was no significant visual or measurable surface appearance change when compared with samples that had not undergone ultrasonic irradiation.

3.6 Chapter Summary
The effect of ultrasonic irradiation in the cleaning of knitted and woven wool fabrics under conditions normally experienced in domestic hand washing have been investigated. The use of ultrasonic irradiation during laundering in a static bath reduces the level of felting shrinkage, relative to hand washing, while still maintaining or improving cleaning efficiency. This improvement in cleaning is obtained with no significant impact on fabric properties including fabric strength, colour, Martindale abrasion resistance or ICI pilling propensity. Ultrasonic irradiation during static cleaning under the same conditions as domestic hand washing is an effective way of improving cleaning and reducing the impact on garment appearance.
4 Ultrasonic Effects on Single Fibre Properties

4.1 Introduction
Ultrasonic irradiation of a cleaning bath is well known as a method for improving surface cleaning of a material. Ultrasonic irradiation of a liquid at a high enough energy level produces cavitation events where bubbles form at a micro scale, grow progressively on each negative acoustic wave until they reach an unstable size and collapse. Both the growth and collapse stage are believed to have an effect on cleaning.

During the growth stage the cavitation bubble grows and shrinks in size with each successive negative and positive acoustic wave respectively. The bubble size oscillation causes micro-streaming which promotes movement of unsaturated cleaning liquor within the liquid and at the surface being cleaned. Cavitation bubble collapse within the liquid causes high temperatures and pressures that help with dissolution and emulsification of a contaminant. Cavitation bubble collapse at a surface produces the same temperatures and pressures combined with a high speed jet of liquid perpendicular to and directed at the surface. This jet of liquid can have a velocity as high as 400 km/hr (Lauterborn and Vogel 1984). It is believed that this jet of liquid is largely responsible for detachment of particles from a surface and rapid dissolution of soluble components from a surface.
An increase in the intensity (power) of ultrasonic irradiation causes an increase in the number of cavitations within an irradiated liquid. An increase in power may be limited, at high irradiation power levels, by a barrier of cavitation bubbles forming near the surface of the ultrasonic irradiation device. The air barrier forms an air cushion that reduces transmission of the ultrasonic wave into the irradiated liquid. Traditionally ultrasonic cleaning baths are designed to irradiate at energy levels low enough that a bubble boundary layer cannot form. Bubble barriers are normally only seen where an ultrasonic horn is used to amplify the intensity of the ultrasonic irradiation.

Ultrasonic irradiation during scouring has been proposed as an alternative to mechanical agitation as it reduces fibre entanglement (Cui 1999; Hurren et al. 2006). A modification to the fibre cuticle structure was observed earlier in this work, during ultrasonic irradiation with the formation of fine cracks in the fibre scale or rounding of the fibre scale tip. The high speed jet of liquid caused by a cavitation bubble collapse next to a fibre surface could be responsible for the cuticle changes.

Wool is a keratin fibre with a complex cellular morphology. The fibres have closely packed cortical cells surrounded by single or multiple layers of cuticle cells (Bradbury 1973; Hearle et al. 1998). Intercellular adhesion is provided by the cell membrane complex (Hearle et al. 1998). Each of the morphological components contains various structural elements which affect the fibre’s tensile, torsional, bending and shear properties. The most common method for evaluating fibre properties is single fibre tensile strength and elongation. This method should be an effective way of evaluating any damage to the internal structural elements of the fibre including the cortical cells and intercellular adhesion.
The previously observed structural changes after ultrasonic irradiation have been to the cuticle scales of the fibre. The scale structure plays a large part in the interaction of a fibre when it is rubbed against another fibre or hard surface. Friction caused by movement of fibre on fibre or fibre on other solid items can lead to surface damage, fibre deformation and even fibre breakage. The extent of damage depends in part on the type of frictional interaction which can include ploughing, rolling, abrasion etc. (Warner 1995). Fibre interaction during fabric wear can result in abrasion fatigue damage and fuzz and pill formation (Goswami et al. 1980; Cooke 1982; Cooke 1985). Measurement of single fibre bending abrasion failure is an effective method for quantifying differences in fibre properties (Liu et al. 2005) and has been used here to search for any effects of the observed scale cracking after ultrasonic irradiation.

Investigations into the effects of ultrasonic irradiation on the wool fibre surface are reported in this Chapter. Fibre surface changes, bending abrasion fatigue, tenacity and elongation to break have been examined. Three separate experiments are presented with separate experimental conditions, results, discussion and conclusions. The overall findings are summarised at the end of the Chapter. The first experiment used scanning electron microscopy to examine the effect of ultrasonic irradiation power level and irradiation liquor chemical composition on morphological changes. The second experiment quantified the effect of ultrasonic irradiation on resistance to fibre bending abrasion fatigue. The third experiment looked at the effect of ultrasonic irradiation on fibre tenacity and elongation to break.
4.2 Fibre Surface Structural Changes

4.2.1 Experimental

4.2.1.1 Fibre and materials
The fibres used for this experiment were from a single Australian merino fleece sourced from the Western District of Victoria, Australia. The fleece had a mean fibre diameter of 21.3 µm and CV of 23.2%. The fibre was pre-scoured to remove surface contaminants. Pre-scouring was done in three sequential baths in a mixture of isopropyl alcohol and petroleum spirit 60-80BP (Sigma-Aldrich Co., USA) at a ratio of 30/70% v/v. The samples were solvent scoured so that the fibre would not be subjected to any aqueous processes before being placed into the ultrasonic horn. Solvent scouring ensured that the fibres were clean and clear of surface contaminants that may have influenced the effect of the ultrasonic irradiation without being structurally or chemically changed by an aqueous treatment.

4.2.1.2 Ultrasonic irradiation
Ultrasonic irradiation was applied using a Sonics Vibra-cell ultrasonic horn (Sonics and Materials Inc., USA). The irradiation frequency of the horn was 20 kHz. Ultrasonic irradiation was undertaken at fixed temperature in a water cooled glass reaction vessel attached to the top of the horn. The intensity of the irradiation was varied over the working range of the horn in increments of 20%. In each trial 0.1±0.0015 g of wool fibres and 10 ml of treatment liquor were placed into a T420 50 ml polypropylene centrifuge container (Simport Scientific, Canada) before the container was partially submerged in the liquid contained in the reaction vessel above the ultrasonic horn. The samples were treated for either 3 or 30 minutes. The treatment liquor was varied for each of the experiments and is detailed in Table 4.1

133
Table 4.1 Experimental conditions

<table>
<thead>
<tr>
<th>Trial No</th>
<th>Treatment liquor composition</th>
<th>Treatment time (min)</th>
<th>Power rating (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Distilled water</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>1.3</td>
<td>Distilled water</td>
<td>3</td>
<td>20</td>
</tr>
<tr>
<td>1.9</td>
<td></td>
<td></td>
<td>80</td>
</tr>
<tr>
<td>2.1</td>
<td>Distilled water</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>2.3</td>
<td>0.5 g/l Hydropol TN450</td>
<td>3</td>
<td>20</td>
</tr>
<tr>
<td>2.9</td>
<td></td>
<td></td>
<td>80</td>
</tr>
<tr>
<td>3.1</td>
<td>Distilled water</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>3.3</td>
<td>0.5 g/l Hydropol TN450</td>
<td>3</td>
<td>20</td>
</tr>
<tr>
<td>3.9</td>
<td>0.2 g/l sodium carbonate</td>
<td></td>
<td>80</td>
</tr>
</tbody>
</table>

4.2.1.3 Fibre surface morphology

Fibre surface morphology microscopy was undertaken using the method detailed in Chapter Two, Section 2.2.1.9.

4.2.2 Results and Discussion

4.2.2.1 Ultrasonic frequency selection

This Section of the chapter utilises 20 kHz ultrasonic irradiation which is different to the 40 kHz used in the remainder of the Chapter. High power (amplitude) ultrasonic irradiation was required to enable rapid determination of fibre cuticle changes. Ultrasonic baths are normally set up to provide low power densities so that cavitation is even throughout the entire bath. To achieve high power level ultrasomics a concentrating device such as an ultrasonic horn is used. An ultrasonic horn is designed to oscillate at one set frequency and most commercial horns have a resonance frequency of 20 kHz.
Due to the inability to obtain a 40 kHz ultrasonic horn a 20 kHz horn was used for these initial experiments.

4.2.2.2 Distilled water
SEM images of the wool fibre samples irradiated in distilled water alone are shown in Figures 4.1, 4.2, 4.3 and 4.4. Figures 4.1 and 4.2 were exposed to the lower power level of 20% for three minutes and exhibit no changes in the morphology of the fibre surface. Figures 4.3 and 4.4 were exposed to 80% power for three minutes and have transverse cracks of the fibre cuticle at regular intervals along the length of the fibre. An increase in amplitude of the standing wave emitted from the ultrasonic horn results in an increase in the number of cavitation events occurring within the bath and has little influence on the intensity or size of the cavitation bubble (Bulat 1974). An increase in the number of cavitation events next to the surface would increase the number of impacts on the fibre surface. Each successive impact would produce cuticle damage hence an increase in cavitation events would result in the presence of cuticle damage. A mechanism of increased power of the cavitation collapse would also support this hypothesis as at low power level ultrasound there are no cracks present and at high power level ultrasound the morphology changes are present.
Figure 4.1 Wool fibre ultrasonically irradiated in trial number 1.3

Figure 4.2 Wool fibre ultrasonically irradiated in trial number 1.3
Figure 4.3 Wool fibre ultrasonically irradiated in trial number 1.9

Figure 4.4 Wool fibre ultrasonically irradiated in trial number 1.9
4.2.2.3 Distilled water with detergent
Figures 4.5, 4.6, 4.7 and 4.8 show SEM images of wool fibres irradiated in distilled water in the presence of a non-ionic detergent. Like the fibres irradiated in distilled water the samples irradiated at a low power level in the presence of detergent undergo no visible change in the cuticle morphology (Figures 4.5 and 4.6). Fibres irradiated under higher power levels in the presence of detergent exhibit two surface morphology changes. Figure 4.7 exhibits a fibre that has had lifting of the tips of the cuticle whereas Figure 4.8 shows a fibre with a high level of transverse and longitudinal cracks over the fibre surface.

At the temperatures employed in these experiments the three minutes of fibre immersion in distilled water liquor would provide only partial surface wetting due to the hydrophobic nature of the fibre epicuticle (Negri et al. 1993). Partial wetting would provide a cushioning layer of air at some places on the fibre surface. It is more likely for air pockets to be more predominant around surface roughness including the region of scale overlap. When detergent is added to the treatment liquor the surface tension of the fibre decreases and the subsequent wetting of the fibre surface increases. As surface wetting increases the energy of cavitation events may be more effectively delivered to the fibre surface. This could increase the level of fibre surface cracking (Figure 4.8). Wetting of the tip of the fibre cuticle scale where it overlaps the next scale enables cavitation to occur close to the overlap. When the jet impacts the surface of the fibre next to the cuticle scale overlap the jet direction is expected to be deflected, by the fibre surface, to parallel with the fibre surface. Some of the liquid jet force would be absorbed by the fibre during the direction change however the jet would still have significant energy in the new direction. This would cause a high speed jet of liquor to impact the cuticle tip and possibly penetrate between
the scale overlap. This bubble growth, collapse and water jet penetrating under the edge of the cuticle tip is felt to be the reason for cuticle tip lifting seen in Figure 4.7.

![Image of wool fibre ultrasonically irradiated in trial number 2.3]

**Figure 4.5** Wool fibre ultrasonically irradiated in trial number 2.3
Figure 4.6 Wool fibre ultrasonically irradiated in trial number 2.3

Figure 4.7 Wool fibre ultrasonically irradiated in trial number 2.9
4.2.2.4 Distilled water, detergent and alkali

SEM images of the fibres that have undergone irradiation in distilled water in the presence of non-ionic detergent and alkali are shown in Figures 4.9, 4.10, 4.11 and 4.12. Even at low power levels there is significant fibre cuticle tip lifting (Figures 4.9 and 4.10). Steeping wool in alkali will break the disulfide bonds that hold the peptide chains together in the keratin structure (Cuthbertson and Phillips 1944). Normally heat is required to accelerate the rate of breakage of the disulfide bond however the increase in cuticle lifting at low irradiation energy could be attributed to acceleration of alkali attack on the wool fibre caused by heat from the cavitation events. Each cavitation event can provide micro points of high temperatures that can be as high as 5000K (Suslick 1990). The detergent could provide the initial fibre scale lifting as mentioned in Section 4.2.2.3 and this would allow the penetration of alkali into the space between the cuticle overlap. The energy from the cavitation event

Figure 4.8 Wool fibre ultrasonically irradiated in trial number 2.9
could increase the rate of attack on the disulfide cross-links within and attaching the cuticle. Alternatively the presence of alkali within the liquor could be enough to modify the properties of the cuticle structure, softening it and allowing the easier penetration of cavitation induced water jets under the overlap point.

Fibres irradiated with 80% power (Figures 4.11 and 4.12) display little to no evidence of fibre cracking or cuticle lifting. A closer examination reveals a sharp edge where cuticle fracture has occurred and the lifted cuticle has separated away from the fibre. A cavitation event close to the raised cuticle could provide the energy to fracture the cuticle plate where it is cantilevered from the fibre. The energy of the cavitation implosion could be enough to snap off the raised cuticle.

A continued bombardment of the fibre structure with high energy ultrasound would be expected to remove the cuticle and break into the internal fibre structure and cause fibrillation of the cortex cells, however Figure 4.13 shows that this is not the case. This fibre has been subjected to 30 minutes of ultrasound at 80% power level. The majority of the cuticle scale structure has been ripped away from the surface of the fibre however it has not exposed the cortex cells. Cuticle flakes were present in the bottom of the treatment vessel after removal from the ultrasonic irradiation. This observation strengthens the hypothesis that the cuticle scales are removed by water jet penetration at the cuticle overlap. The long plate shape of the cuticle allows excellent leverage for the liquid jet to lever off the cuticle. Once the length of the cuticle is reduced then this leverage is reduced hence total cuticle removal is thwarted.
Figure 4.9 Wool fibre ultrasonically irradiated in trial number 3.3

Figure 4.10 Wool fibre ultrasonically irradiated in trial number 3.3
Figure 4.11 Wool fibre ultrasonically irradiated in trial number 3.9

Figure 4.12 Wool fibre ultrasonically irradiated in trial number 3.9
4.2.3 Conclusions
The amount of surface damage is increased by increased irradiation power. The presence of detergent reduces the surface tension of the fibre liquor interface enabling cavitation events to occur closer to the fibre surface which in turn causes higher surface damage. The alkali attack of disulphide bonds within the fibre cuticle may be accelerated by heat generated by cavitation events.

4.3 Single Fibre Bending Abrasion

4.3.1 Experimental
4.3.1.1 Fibre and materials
The fibre used for this experiment was from an Australian merino wool top that had been scoured, carded and combed. The fibre was sourced from the Riverina district of Southern New South Wales, Australia. The top had a mean
fibre diameter of 19.6 μm and was separated into six samples of 20.0 g each. Each of the samples was washed for 90 minutes at 60°C using either no agitation or ultrasonic irradiation. The chemicals used in this research were Hydropol TN450 (Huntsman International LLC., USA), sodium carbonate, ammonium sulphate and acetic acid (all from Sigma-Aldrich Co., USA).

4.3.1.2 Experiment conditions
The ultrasonic and control samples were treated in identical liquors. The treatment liquor was made up in one container before being halved for each of the experiments. The pH was measured after the addition of fibre before the start of ultrasonic irradiation or timing of the control experiment. The details of the treatment liquors for each of the experiments are given in Table 4.2.

**Table 4.2 Treatment liquor conditions**

<table>
<thead>
<tr>
<th>Method number</th>
<th>Treatment liquor composition</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkaline Ultrasonic</td>
<td>0.2 g/l Sodium carbonate (Na₂CO₃)</td>
<td>8.62</td>
</tr>
<tr>
<td></td>
<td>0.1 g/l Ammonium sulphate</td>
<td></td>
</tr>
<tr>
<td>Alkaline Control</td>
<td>0.2 g/l Sodium carbonate (Na₂CO₃)</td>
<td>8.79</td>
</tr>
<tr>
<td></td>
<td>0.1 g/l Ammonium sulphate</td>
<td></td>
</tr>
</tbody>
</table>
Neutral Ultrasonic
0.5 g/l Hydropol TN450
0.6 g/l Ammonium sulphate

Neutral Control
0.5 g/l Hydropol TN450
0.6 g/l Ammonium sulphate

Acidic Ultrasonic
0.5 g/l Hydropol TN450
0.2 g/l Acetic Acid

Acidic Control
0.5 g/l Hydropol TN450
0.2 g/l Acetic acid

After treatment the samples were rinsed under cold running water before the fibre was squeezed in an SDL pad mangle (SDL Atlas Inc., England) to remove excess liquor. Samples were then dried for one hour at 105°C in a fan forced oven before conditioning for more than 24 hours at 20±2°C temperature and 65±2 % humidity.

The ultrasonic bath used was a Decon FS300B (Decon Laboratories Ltd., United Kingdom). The ultrasonic bath has a working frequency of 35-45 KHz and 400 Watt peak power. Temperature control was achieved using a Thermoline L+M Unistat heater circulator (Thermoline Scientific Pty. Ltd., Australia).
4.3.1.3 Fibre bending abrasion preparation

Figure 4.14 shows the method for preparing single fibres at a set gauge length for the single fibre tensile and bending abrasion tests. Single wool fibres were prepared for abrasion testing on a 100 µm thick clear plastic film, made black in a photocopier to ease in the identification of the fibres. A piece of double sided tape was laid down one side of the slide and then a second one was placed exactly 45 mm away from the first on the other side of the slide. This separation provided the 45 mm gauge length of the test to be performed. Little marks separated by 8 mm were then placed next to the tape down the full length to provide a guide for laying up the fibres.

![Diagram of fibre preparation method](image)

**Figure 4.14** Single fibre test preparation method

Each fibre was randomly selected from the top and placed on the tape on one side so that the fibre protruded perpendicular from the tape. The other end was then fixed to the other tape so that it was held perpendicularly between the two
pieces of tape. After all of the fibres had been laid on the slide a second piece of double sided tape was placed directly over the top of the first. A piece of masking tape was placed over the top of the double sided tape to finish. Fibre details were written onto the masking tape at each fibre location.

**4.3.1.4 Determination of fibre orientation**
The tip direction of each fibre was determined using an Olympus SZX 12 down-lit optical microscope (Olympus Corporation, Japan) at 500X magnification. The direction of the fibre was identified by writing either tip or base onto the masking tape adjacent to the fibre. The plastic was then removed from the back of the fibre in preparation for fibre diameter measurement.

**4.3.1.5 Fibre diameter measurement**
Fibre diameter and its distribution along the length of each single fibre, was measured using a SIFAN II Single Fibre Analyser (BSC Electronics, Australia). The gauge length on the machine was set at 44 mm and the tension applied to the fibre during diameter measurement was 0.089 cN. The fibre was placed into the SIFAN II with the base in the upper jaw. After measurement, the diameter versus length measurements for each of the fibres was saved into a numbered comma separated value (CSV) file for future reference. After testing, the tension was removed from the fibre and the fibre was removed from the SIFAN II and placed into the fibre abrasion tester.

**4.3.1.6 Fibre bending abrasion measurement**
Each fibre was mounted in a FIBRESTRESS abrasion tester (Textechno H. Stein GmbH & Co KG, Germany) to evaluate its bending abrasion fatigue. The experimental setup and parameters are shown in Figure 4.15. During fibre bending abrasion testing the base of each fibre was clamped on to the oscillating clamping strip. The other end was attached to a free hanging 800 mg weight. The fibre was bent at 90° over a 50 μm diameter wire. The
oscillating clamping strip was moved at a frequency of 5 Hz and displacement of 10.0 mm and caused bending/abrasion movement of the fibre over the wire. The oscillation stopped when all of the test fibres had broken. Twenty four fibres were measured during each run of the abrasion tester. The number of cycles to break for each fibre was recorded automatically on break. The bending abrasion properties for 200 fibres were measured for each of the experimental conditions.

**Figure 4.15** Fibre path diagram on Textechno FIBRESTRESS abrasion tester

**4.3.1.7 Surface morphology**
Surface morphology images were undertaken using the same method as that given in Section 4.2.1.3

**4.3.2 Results and Discussion**
Figures 4.16, 4.17 and 4.18 show microscopy images of the treated fibres used in the following two experiments. These images were taken to verify that cracking was evident on the surface of the fibre. Fibre surface cracking is similar to that seen in previous experiments.
**Figure 4.16** Alkaline pH fibre surface image

**Figure 4.17** Neutral pH fibre surface image
Figures 4.19, 4.20 and 4.21 show the results of the single fibre bending abrasion tests. There was no significant difference between the bending abrasion fatigue properties of the fibres that have undergone ultrasonic irradiation when compared to the control samples. This result was not expected as Liu et al. (Liu et al. 2005) found that the mechanism of fibre failure in bending abrasion fatigue first starts with peeling away of the cuticle cells from the fibre to expose the cortical cells within. It was expected that the damage to the cuticle scale structure caused by ultrasonic irradiation would have increased the rate at which the cuticle cells peeled off the fibre and hence accelerated the rate of failure.

These results could be explained in two ways. The first explanation is that the peeling of the cuticle structure has little influence on the bending abrasion fatigue failure of a wool fibre. The second explanation is that the changes to the cuticle structure do not significantly increase the failure rate of the cuticle when subjected to bending abrasion fatigue.
Bending abrasion resistance is an important factor in the carding and top-making of fibres during fibre spinning. It can be assumed that the negligible difference in bending abrasion would result in no effect on the yields achieved after carding and top-making. On the contrary, previous work has shown that there is less fibre entanglement for the same level of cleaning when ultrasonic irradiation is adopted instead of a rake scour action (Hurren et al. 2006). These abrasion results show that the use of ultrasonic irradiation during scouring will result in better carding and top-making yields and better fibre length after top-making due to reduced fibre breakage.

Figure 4.19 Alkaline pH abrasion results
4.3.3 Conclusions
Despite some visible changes to the cuticle, ultrasonic irradiation at a fixed frequency and fixed intensity has been shown to have a negligible effect on the bending abrasion resistance of wool fibres scoured in acidic, neutral and
alkaline scour liquors. Chapter Two, Section 2.2 has shown that a similar power level of ultrasonic irradiation on a similar mass of wool under identical temperature and chemical conditions as the alkaline liquor has been shown to improve scouring efficiency.

4.4 Single Fibre Tensile Testing

4.4.1 Experimental
4.4.1.1 Fibre and materials
Fibre, materials and ultrasonic treatment conditions were the same for this experiment as those used for single fibre bending abrasion testing (Section 4.3.1.1 and 4.3.1.2). The fibre treatments were conducted in tandem so that results could be cross referenced between the two experiments. Fibres were mounted for single fibre tensile testing using the system adopted for single fibre abrasion testing (Section 4.3.1.3) however a change was made to allow a gauge length of 25mm.

4.4.1.2 Single fibre tensile testing
The single fibre tensile testing was conducted on a SIFAN II using a gauge length of 25 mm and at an extension rate of 300 mm/min. The experiment set up and parameters are shown in Figure 4.22. The SIFAN II was set at a gauge length of 25 mm and a pretension force of 0.089 cN for the diameter measurements. The diameter variation along the length of the fibre was measured first, the pretension was then released and the fibre pulled to break. The crosshead movement rate was 300 mm/min for both the diameter measurements and pull to break measurements. All of the parameters measured were saved into a CSV file for future reference. The tensile properties of 200 fibres were measured for each of the experiment conditions. The tenacity was
calculated using the Equation 4.1 and the linear density was calculated using Equation 4.2.

\[
Tenacity = \frac{F}{LD}
\]  

(4.1)

Where \( F \) is the force to break in cN and \( LD \) is the linear density in tex (g/1000m).

\[
LD = \frac{\rho \times \pi \times d^2}{40}
\]  

(4.2)

Where \( \rho \) is the density of wool (1.31 g/cm\(^3\)) in g/cm\(^3\) and \( d \) is the minimum diameter of the fibre tested in µm.

Figure 4.22 SIFAN II experiment set up and parameters

4.4.2 Results and Discussion
Table 4.3 shows the results of the single fibre tensile tests. There is no significant difference between the ultrasonically irradiated samples or control samples for any of the pH conditions. Figures 4.23, 4.24 and 4.25 show the
strain versus tenacity distribution for each of the single fibre tensile tests. These results show that there have been negligible changes to the cortical cells or intercellular adhesion because the chemical break down of the cortical cells and intercellular adhesion generally results in lower tenacity due to cortical cell fibrillation and individual failure (Hearle et al. 1998).

Table 4.3 Mean single fibre tenacity and strain results

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<tr>
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<th>Alkaline conditions</th>
<th>Neutral conditions</th>
<th>Acidic conditions</th>
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<tr>
<td></td>
<td>Tenacity (cN/tex)</td>
<td>Strain (%)</td>
<td>Tenacity (cN/tex)</td>
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<tr>
<td>Ultrasonic</td>
<td>Mean 35.57</td>
<td>43.00</td>
<td>Mean 38.24</td>
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<td></td>
<td>(SD) (8.3)</td>
<td>(12.0)</td>
<td>(SD) (7.6)</td>
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<tr>
<td>Control</td>
<td>Mean 35.59</td>
<td>42.80</td>
<td>Mean 34.18</td>
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<tr>
<td></td>
<td>(SD) (8.7)</td>
<td>(12.1)</td>
<td>(SD) (9.0)</td>
</tr>
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</table>
Figure 4.23 Alkaline pH tensile results

Figure 4.24 Neutral pH tensile results
4.4.3 Conclusions
Despite some visible changes to the cuticle, the level of ultrasonic irradiation used has been shown to have negligible effect on the tenacity and strain to break of wool fibres scoured in acidic, neutral and alkaline scour liquors.

4.5 Chapter Summary
The results of this Chapter show that fibre surface damage increases with increased ultrasonic irradiation power. A detergent present in the cleaning liquor reduces the surface tension of the fibre liquor interface enabling better transfer of the energy from the cavitation event to the fibre which results in higher surface damage. Surface damage is further accelerated by the presence of an alkali and this may be attributed to cavitation induced heating increasing the rate of alkali attack of disulphide bonds within the fibre cuticle. High force liquid jetting under the cuticle overlap from ultrasonic induced cavitation is most likely hypothesis for scale detachment. Long exposure times to 80%

Figure 4.25 Acidic pH tensile results
power level 20 kHz ultrasound will only remove the cuticle structure and not penetrate into the fibre cortex.

Despite some visible changes to the cuticle, ultrasonic irradiation at a fixed frequency and fixed intensity has been shown to have a negligible effect on the bending abrasion resistance, tenacity and strain to break of wool fibres scoured in acidic, neutral and alkaline scour liquors. When combined with findings in previous Chapters it is clear that the use of ultrasonic irradiation for the scouring of raw wool is a potential alternative to rake wool scouring as it has the same dirt and grease removal ability with less felting entanglement of fibre and minimal fibre damage.
CHAPTER FIVE

5 Ultrasonic Assisted Dyeing of Wool Fibres

5.1 Introduction

Wool is a complex fibre composed primarily of a group of proteins known as keratins. The two main physical features of a wool fibre are the internal cortex and the external cuticle. Cuticle cells cover the exterior of the wool fibre, and are an important factor in the dyeing process. The cells are flat and plate like in profile and overlap each other similar to scales on a fish. The cuticle cell surfaces are moderately hydrophobic making them a barrier to dye penetration. For dye to migrate from the dye bath into the fibre it must negotiate a path between the scales (Hall 1937; Leeder et al. 1985). Elevated temperatures are employed to increase the gaps between the scale structures to enable dye penetration into the inner regions of a wool fibre due to a swelling of the fibre. To evaluate the number of dye paths into a wool fibre, low fixed temperature isothermal dyeing is employed as the rate of dyeing is reduced due to reduced fibre swelling at the lower immersion temperature.

The mechanism of dyeing can be summarised in terms of three steps (Simpson 2002): movement of dye from dye bath to fibre surface, movement of dye from the fibre surface into the fibre and migration of dye within the fibre. The rate of dye absorption is governed by the dye interaction with the fibre surface. At low temperatures the limiting factors in the rate of wool dyeing is the size and number of scale junctions and the size of the dye molecule. An increase in the number of scale junctions or a decrease in the size of the dye will result in an increase in the rate of dye uptake.
Ultrasound has been used by a number of researchers to improve dyeing performance. This is normally achieved by an increase in the dye uptake and/or accelerated dyeing rates (Vajnhandl and Marechal 2005). Ultrasonic irradiation has been found to improve one of the above factors in a variety of textiles including leather (Sivakumar and Rao 2001; Sivakumar and Rao 2004; Sivakumar et al. 2005), cotton (Akalin et al. 2004; Kamel et al. 2007; Vankar et al. 2007), silk (Vankar et al. 2008) nylon (El-Shishtawny et al. 2003; Kamel et al. 2003) and wool (Kamel et al. 2005). A number of hypotheses have been proposed for why ultrasonic irradiation contributes to an increase in dye uptake rate and dye adsorption. These include: increased energy within the dye-bath, dye de-aggregation, surface degassing and surface boundary layer reduction. Each of these has been expanded on below.

Ultrasonic irradiation of a chemical reaction can provide acceleration in the rate of reaction via a phenomenon known as sono-chemistry (Suslick 1989). Ultrasonic irradiation produces localised areas of increased temperature and pressure. This increased energy may enhance the movement of dye from the fibre surface into the fibre structure (Sivakumar and Rao 2003; Moholkar and Warmoeskerken 2004; Sivakumar et al. 2005).

Dye particles are normally supplied in the form of a fine powder. When dissolved in water agglomeration of the dye can occur with large particles of multiple dye molecules clumping together. De-aggregation of larger aggregates due to cavitation provides smaller dye particles or individual dye molecules well dispersed within the dye solution. Smaller dye particle size assists diffusion as dyes can pass into the structure with less hindrance and with less energy (Kamel et al. 2003; Lee et al. 2003).
A gas layer on the fibre surface or within the fibre can provide a barrier for dye penetration. Ultrasonic irradiation of the dye liquor increases the rate of surface wetting as the cavitation liquor jets penetrate the boundary layer and drive off surface bound air pockets. A fully wetted surface increases the dye and dye liquor entry points to a fibre and increases the expulsion of entrapped gas molecules within the fibre. Both of these will increase the rate and amount of dye uptake (Sivakumar et al. 2008).

On implosion the cavity collapses and high speed jets are released increasing the turbulent flow of liquid next to the fibre surface. In a normal flowing liquid/solid interface there is a boundary layer of stationary liquor. This can reduce the dye concentration at the surface limiting dyeing rate. Ultrasonic irradiation reduces the liquid/solid interface boundary layer enabling an increased rate of dye transfer onto the fibre surface (Moholkar and Warmoeskerken 2004).

Earlier work in the scouring of greasy wool fibre with ultrasonics (Hurren et al. 2006) led to the observation that ultrasonic treatment of wool fibres resulted in micro-cracking of cuticle scales. This cracking behaviour has been investigated in detail in Chapter 4 of this thesis. Micro-cracking of the scale structure could increase the dye pathways into the fibre enabling a more rapid rate of dye uptake at lower dyeing temperatures. No publications were found on the effect that changes in surface morphology had on dyeing rate. This Chapter aims to determine if ultrasonic induced cuticle changes affect the rate of dye uptake and to quantify if this is a component of the improvement seen in previous ultrasonic assisted research.
Investigations into the effects of surface cracking from pre-treatment with ultrasonic irradiation on wool dyeing rate and uptake are reported in this Chapter. Low temperature isothermal dyeing is used to appraise changes in dye exhaustion rates. Three separate experiments are presented each with its own experimental conditions, results, discussion and conclusions. The overall findings are summarised at the end of the Chapter. The first experiment examines the effect of ultrasonic pre-treatment of a fabric under normal scouring conditions on subsequent dye exhaustion rate. The second experiment quantifies the effect of the composition of the pre-treatment liquor used during ultrasonic irradiation on subsequent dye exhaustion rate. The third experiment looks at the contribution of the level of fibre cracking of the cuticle structure to dyeing rate increase during ultrasonically assisted dyeing.

5.2 Ultrasonically Pre-Treated Wool Dyeing

5.2.1 Experimental

5.2.1.1 Fabric specifications and preparation
The fabric used in this experiment and the preparation method was the same as that used in Chapter Three, Section 3.2.1.1. Woven fabric was selected for the trials as it provided an easier substrate for colour measurement.

5.2.1.2 Ultrasonic treatment
The test fabric was subjected to ultrasonic irradiation at 60°C for 60 min using a liquor ratio of 20:1 in 0.5 g/l Hydropol TN450 (Huntsman International LLC., USA) and 0.2 g/l sodium carbonate (Sigma-Aldrich Co., USA). Fabrics were placed into 2.0 l Pyrex beaker suspended in the ultrasonic bath by a pipette stand and clamp. The control fabric was subjected to exactly the same conditions but without the ultrasonic irradiation. The fabrics were then padded to a liquor content of 80% in a Rapid PA0 pad mangle (Rapid Labortex
Co.LTD., Taiwan) before being rinsed in warm water twice, with padding after each rinse. After the final padding they were dried at 105°C for one hour before being conditioned according to AS2001.1 1995 (Standards Australia 1995).

5.2.1.3 Ultrasonic bath
The ultrasonic bath used was the same as that described in Chapter Two, Section 2.2.1.3.

5.2.1.4 Isothermal dyeing
Samples of 1.400±0.005 g each, cut from the pre-treated fabric, were isothermally dyed at 40°C in an Ahiba Nuance Top Speed laboratory dyeing machine (Datacolor International, USA). Each bath contained 0.2% w/w Lanaset Blue 2RA (Huntsman Textile Effects, Singapore) dissolved in distilled water. A large volume of the dye solution was prepared so that all starting baths had the same dye concentration and pH. 100ml of the dye solution was placed into each dye vessel. The pH of the dye liquor in the presence of a fabric sample at the start of the dyeing was 6.85. The 100 ml of dye liquor at 40°C was placed by pipette into each of the dye vessels, the fabric was added to each vessel, the lid placed on each vessel and the vessels placed into the Ahiba Nuance dyeing machine. Samples were rotated at 20 revolutions per minute with the direction reversed every three minutes.

Dye vessels for the ultrasonically treated fabric and control fabric were removed every 25 minutes from the Ahiba Nuance dyeing machine. Dye progress in the sample was halted by removal of the fabric from the dye solution and rinsing in cold water immediately after the dye vessel was removed from the machine. Samples were taken at the 25, 50, 75, 100 and 125 minute mark. Three repeats were conducted for each dyeing temperature for the ultrasonic treated and control fabrics. Each dyeing was in a separate vessel.
and separate dye bath dyeing was used for each repeat for each fabric for each
time iteration (30 dyeings in total). The fabrics were then padded to a liquor
content of 83% in a Rapid PA0 pad mangle (Rapid Labortex Co.LTD.,
Taiwan) before being rinsed in warm water twice, with padding after each
rinse. After the final padding they were dried at 105°C for one hour before
being conditioned according to AS2001.1 1995 (Standards Australia 1995) in
preparation for colour measurement.

5.2.1.5 Fabric colour measurement
Colour depth was evaluated in terms of K/S values and these were calculated
using Kubelka–Munk’s equation (Equation 5.01).

\[ K/S = \frac{(1 - R)^2}{2R}, \quad (5.01) \]

\( R \) is the reflectance.

The reflectance values were measured with a Datacolor SF600
spectrophotometer (Datacolor International, USA). Measurements were taken
using the standard illuminant D65 and a LAV aperture with specular included
and 10º field of view. Five measurements were taken for each fabric sample
with the fabric moved to a new location for each capture.

5.2.2 Results and Discussion
This experiment applied an ultrasonic treatment to the fabric before dyeing and
none during dyeing. An increase in the rate of colour depth change for the
ultrasonically irradiated fabric would indicate that the cracking of the scale
structure, or other changes induced by the cavitation, has increased the number
of pathways or ease of dye penetration into the fibre. Dye penetration normally
occurs between the overlap of the scales. An even distribution of surface
cracking of fibres in the test fabric would be identifiable by an increase of K/S
values for the cracked fibre, when compared to the fibre without cracks, as dyeing time increased.

Figure 5.1 shows the K/S values for the wool fabric at 25 minute intervals during isothermal dyeing. A greater increase in K/S is seen in the sample that had undergone ultrasonic laundering as the dyeing time increases. The increased dye uptake can most probably be attributed to the surface cracking as the dye is able to diffuse into the fibre through the cracks as well as between the overlap of the scales.

In previous ultrasonically assisted dyeing work on wool (Kamel et al. 2005) it was proposed that an increase in the rate of dye uptake was provided by exposure to ultrasonic energy during the dyeing process. In their work they irradiated the fabric and dye during the dyeing process however in this work the fabric is irradiated in a separate bath before the dyeing process. The micro cracking of the surface structure prior to dyeing is associated with an increase in the dyeing rate and would be expected to be a component of the rate increase seen by the previous work (Kamel et al. 2005).

The presence of fibre cracking would have an effect on the wet fastness of some dyes. They would have a large effect on the wet fastness of acid dyes, a moderate to small effect on premetalised dyes and little to no effect on reactive dyes. With the requirements of machine wash wool fabrics increasing the main dye class used is reactive dyes with some premetalised dyes as acid dyes cannot meet the wash fastness specifications in wools that have had significant cuticle modification to provide shrink resistance.
5.2.3 Conclusions
Ultrasonic treatment of wool fibres in an alkaline bath with detergent causes an increase in the rate of dye adsorption (increased $K/S$). Dye adsorption into the fibre would appear to be assisted by the fine cracks that occur on the fibre cuticle after ultrasonic irradiation.

5.3 Ultrasonic Pre-treatment Liquor Composition Effect on Dye Uptake

5.3.1 Experimental

5.3.1.1 Fabric specifications and preparation
The fabric used in this experiment and the preparation method is the same as that used in Chapter Three, Section 3.2.1.1

5.3.1.2 Pre-treatment
The fabric was subject to three different pre-treatments at a 100:1 liquor ratio for 60 minutes at 60°C. Fabrics were placed into 2.0 l Pyrex beaker suspended
in the ultrasonic bath by a pipette stand and clamp. The first fabric was ultrasonically irradiated in deionised-water (DI water) only. The second fabric was ultrasonically irradiated in DI water containing 0.5 g/l Hydropol TN450 (Huntsman International LLC., USA) and 0.2 g/l sodium carbonate (Sigma Aldrich). The third fabric (control) was subjected to a treatment liquor with the same composition as that used for the second fabric however the sample was not subjected to ultrasonic irradiation. After pre-treatment the fabrics were rinsed thoroughly, padded to remove excess water, and dried at 105°C for 10 minutes. Following drying, fabrics were left to condition for 24 hours at 20°C and 65% humidity. The fabric was then cut into 2.0±0.005 g samples ready for dyeing.

5.3.1.3 Ultrasonic bath
The ultrasonic bath used in this experiment is the same as that detailed in Chapter Two, Section 2.2.1.3.

5.3.1.4 Dyeing
The dyeing method used was the same as that detailed in Section 5.2.1.4 apart from the mass of fabric used (2.0±0.005 g), the liquor ratio (50:1), the measured pH for the dye solution before addition to the wool fabric (7.76) and deletion of the 125 minute dye sample.

5.3.1.5 Dye exhaustion measurement
Absorbance of the dye bath liquor before and after dyeing was undertaken using a Varian Carey 3 UV/Vis spectrophotometer (Varian Inc. Scientific Instruments, USA). The wavelength of maximum absorption (589 nm) was determined by scanning the initial dye solution from 380-700 nm. The absorption of each dye solution after dyeing was measured with the instrument in single wavelength mode at 589 nm. The dye bath liquor was cooled to 20°C
before measurement and five scans were conducted for each solution. The percentage dye exhaustion was calculated using Equation 5.2

\[
S_b = \frac{A_0 - A_t}{A_0} \times 100
\]  

(5.2)

Where \( A_0 \) is the absorbance of the dye liquor before fabric is added, and \( A_t \) is the absorbance at end dyeing finish time.

5.3.1.6 Fabric colour measurement
Fabrics were measured for colour using the same method as that detailed in Section 5.2.1.5.

5.3.2 Results and Discussion
5.3.2.1 Dye uptake
The rate of dyebath exhaustion versus time for each of the pre-treatments is shown in Figure 5.2. The type of pre-treatment that the fabric is given is seen to have a significant effect on the outcome of the dyeing process. Ultrasonic pre-treatment improves the rate of dye uptake. The two fabrics that received ultrasonic pre-treatment achieved higher dye exhaustion than the fabric without pre-treatment. The fabric ultrasonically irradiated in the presence of detergent has a faster rate of dye exhaustion than the other two treatment methods. The detergent lowers the surface tension of the water which increases fibre wettability. As the wool fibre surface is hydrophobic, this effect is relatively significant. Increased wettability allows for superior transmission of ultrasonic waves throughout the fabric (Datar et al. 1996b) (Datar et al. 1996a) (Karaboga et al. 2007), and therefore it would be expected that this would be the same in a loose fibre environment. A higher transmission of ultrasonic irradiation into the fibre is expected to result in a higher degree of cracking in the fibre surface. Electron microscope images of this micro-cracking of the
fibre cuticle as a result of ultrasonic irradiation have been shown in Chapter Four, Section 4.2 of this work. An increase in the cuticle damage of fibre irradiated in the presence of a detergent was observed when compared with a fibre irradiated in DI water only. The exhaustion curves shown in Figure 5.2 show that the increased dyeing rate is associated with an increase in damage rather than because the presence of a detergent provided a cleaner fibre as all of the fabrics were cleaned in an alkaline scour before the experiments were undertaken.

![Figure 5.2 Dye exhaustion versus dyeing time](image)

**5.3.2.2 Fabric colour**

Figure 5.03 shows the K/S values for each of the treatment conditions with respect to dyeing time. The results follow the same trend as that seen in the dye liquor exhaustion curves (Figure 5.2). This confirms that the surface cracking is associated with an increase in dye adsorption onto the fibre.
5.3.3 Conclusions

The presence of an alkali and detergent during pre-treatment with ultrasonic irradiation increases the fabrics subsequent dye exhaustion rate when dyed with the pre-metallised dye Lanaset Blue 2RA. The increased level of cracking contributed to by the presence of detergent and alkali during ultrasonic irradiation appears to explain the increase in dye exhaustion rate. Cracking is present in the water only ultrasonic treated fabric but it is less than the fabric that was irradiated in the presence of detergent.

Figure 5.3 Increase in fabric colour versus dyeing time
5.4 Ultrasonically Assisted Dyeing Compared With Ultrasonic Pre-treatment

5.4.1 Experimental
5.4.1.1 Fabric specifications and preparation
The fabric used in this experiment and the preparation method was the same as that used in Chapter Three, Section 3.2.1.1. After conditioning, fabric samples of 2.000±0.005 g were prepared for each individual dyeing.

5.4.1.2 Treatment paths
Three different treatment paths were used:

Path 1 Dyeing without ultrasonic agitation

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Minutes standing in 55°C water

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Minutes dyeing at 55°C

Path 2 Dyeing with ultrasonic pre-treatment

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Minutes of ultrasonic treatment in 55°C water

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Minutes dyeing at 55°C

Path 3 Dyeing with ultrasonic irradiation

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Minutes standing in 55°C water


The pre-treatment liquor was deionised water without detergent or alkali. Each time in each path was repeated three times.

**5.4.1.3 Pre-treatment**
The fabrics were subject to two different pre-treatments at 55°C in a 250 ml Pyrex conical flask at a 50:1 liquor ratio. Pre-treatment was conducted in a Stuart shaking water bath SBS40 (Bibby Scientific Limited, United Kingdom) for pre-treatment without ultrasonic irradiation or in a Deacon FS300B ultrasonic bath for pre-treatment with ultrasonic irradiation. The action of the Stuart shaking water bath was orbital in motion and was set to 20 revolutions per minute for both the pre-treatment and dyeing steps. The ultrasonic bath and power levels were the same as those used in the two previous experiments (as detailed in Chapter Two, Section 2.2.1.3). Pre-treatment vessels were removed after 20, 40, 60, 80 and 100 min and the fabric removed from the treatment solution and padded in a Rapid PA0 pad mangle (Rapid Labortex Co.LTD., Taiwan) to remove excess water. Fabrics were then retained for the appropriate dyeing step.

**5.4.1.4 Dyeing**
Fabric samples were isothermally dyed at 55°C in a 250 ml Pyrex conical flask at a liquor ratio of 50:1. Dyeing was conducted in a Stuart shaking water bath SBS40 for dyeing without ultrasonic irradiation or in a Deacon FS300B ultrasonic bath for dyeing with ultrasonic irradiation. Each bath contained 0.2% w/w Lanaset Blue 2RA (Huntsman Textile Effects, Singapore) dissolved in distilled water. A large volume of the dye solution was prepared so that all starting baths had the same dye concentration and pH. 100ml of the dye solution was placed into each dye vessel. The pH of the dye liquor in the
presence of a fabric sample at the start of the dyeing was 7.23. The 100 ml of dye liquor at 55ºC was placed by pipette into each of the dye vessels, the fabric was added to each vessel just before the vessel was added to the dyeing bath. Flasks held in the ultrasonic bath were suspended statically from above by a burette stand, boss-head and clamp.

Dye vessels were removed every 20 minutes. Dye progress in the sample was halted by removal of the fabric from the dye solution and rinsing in cold water immediately after the dye vessel was removed from the machine. Samples were taken at 20, 40, 60, 80 and 100 minutes. The fabrics were then padded to a liquor content of 81% in a Rapid PA0 pad mangle before being rinsed in warm water twice, with padding after each rinse. After the final padding they were dried at 105ºC for one hour before being conditioned according to AS2001.1 1995 (Standards Australia 1995) in preparation for colour measurement.

### 5.4.1.5 Dye exhaustion measurement

The dye exhaustion method used was the same as that detailed in Section 5.3.1.5.

### 5.4.2 Results and Discussion

Figure 5.4 shows the % dye exhaustion versus treatment time for the isothermal dyeing. The difference between pre-treatment in DI water with and without ultrasonic irradiation is small. This was expected as electron microscope images in Chapter Four, Section 4.2 showed that ultrasonic irradiation in the presence of DI water at low power levels produces minimal to no fibre cuticle damage. The power level in the ultrasonic bath used in this experiment is high enough to provide a small amount of fibre cuticle change
but not high enough to provide significant amounts of change in water alone. If pre-treatment was undertaken in the presence of a detergent or detergent alkali combination then this difference would have been larger, however, the complexity of removing the detergent and alkali from the sample before dyeing would have significantly complicated the experiment.

The exhaustion rate of the sample that underwent ultrasonic irradiation during dyeing is significantly higher than the other two samples. The presence of ultrasonic irradiation during dyeing increases the exhaustion rate and provides a significant component of the improvement seen in ultrasonically assisted dyeing. Cracking from ultrasonic exposure (either as pre-treatment or during dyeing) provided 0-20% of the improvement in dye uptake depending on the dyeing time (1 % for 20 min, 11 % for 40 min, 12 % for 60 min, 20 % for 80 min and 24 % for 100 min).

![Dye exhaustion at an isothermal dye temperature of 55°C](image)

**Figure 5.4** Dye exhaustion at an isothermal dye temperature of 55°C
5.4.2.1 Repeatability
As the complexity of the dyeing experiments was increased the repeatability of the experiments was compromised. The experiments undertaken in Section 5.2 had one ultrasonic treatment only where all of the fabrics to be dyed were subjected to the same treatment. These experiments showed very good repeatability and agreement with the hypothesis. The experiments undertaken in Section 5.3 had an increased number of ultrasonic treatments. For these treatments the initial repeatability and conformity to previous results was lower. Significant care had to be taken to ensure that the treatment liquor and ultrasonic bath liquor had been degassed to the same level before treatment was undertaken. A slight change in the level of liquor degassing significantly changed the uptake of the dye and it is proposed that this is because the level of cracking is reduced with increased gas levels. In Section 5.4 an individual ultrasonic treatment was conducted for each treated sample. Extreme care had to be undertaken to ensure that the liquor was degassed and that the treatment vessel was placed in the same location within the ultrasonic bath. A number of experiments were discarded and the work repeated with more care in order to obtain a set of repeatable results. The effects were exaggerated because difference in exhaustion during a low temperature isothermal dyeing was being examined. Exhaustion of the dyeing at normal dyeing temperatures would be difficult to examine. Ultrasonic irradiation during dyeing increases the rate of dyeing or lowers dyeing temperature but generally has no effect on the total amount of dye adsorbed by the fibre.

5.4.3 Conclusions
Cuticle cracking resulting from ultrasonic irradiation contributes to an increase in dye exhaustion during isothermal dyeing at 55°C by up to 20% depending
on the length of the dyeing. The level of degassing and the position of the sample within the ultrasonic bath during ultrasonic irradiation have a significant influence on the improvement in dye exhaustion rate.

### 5.5 Chapter Summary

This Chapter shows that cracking of the fibre cuticle contributes to an increase in dyeing rate when dyeing is undertaken with the pre-metallised dye. Fibre cracking is caused by ultrasonic implosions close to the fibre surface and is directly influenced by treatment power and chemicals present within the treatment liquor. Dyeing rate increases are proportional to the level of cracking on the fibre surface. Fibres ultrasonically irradiated in water only show low levels of dye exhaustion rate improvement when compared to fibres irradiated in the presence of a detergent and alkali.

Cuticle cracking only provides a small component of the overall improvement in dye exhaustion during isothermal dyeing at 55ºC with a contribution of 0-20% depending on the duration of the dyeing. Significant care needs to be taken to ensure that samples have the correct level of degassing and are consistently placed in the same place within the treatment bath otherwise repeatability is significantly compromised.
6 Conclusion and Future Work

6.1 Conclusion

This work has investigated the use of ultrasonic irradiation within a bath of water, wool and detergent as a means of improving contaminant removal while lowering cleaning energy, water contamination and chemical use. It examined the effect of ultrasonic irradiation on the structure and properties of wool fibres and the properties of fabrics made from these fibres. The areas of wool fibre scouring, ultrasonic fabric laundering, ultrasonic effects on single fibre properties and ultrasonically assisted wool dyeing were investigated.

Ultrasonic irradiation during greasy wool scouring provides a number of improvements. Ultrasonic irradiation instead of a rake scouring action assists with grease removal and enables a reduction in the detergent and temperature required for scouring. Ultrasonic irradiation causes less movement of the fibres than the rake action resulting in less fibre entanglement. Less fibre entanglement is confirmed by less fibre breakage or diameter change during subsequent carding.

Fibre colour is not significantly affected by ultrasonic irradiation during scouring. Micro-cracking of the fibre cuticle is observed in samples that have been ultrasonically irradiated during scouring.

Wool fibre present in an ultrasonic scouring bath absorbs ultrasonic irradiation. Absorption increased with increasing wool fibre with no erosion of 30µm aluminium foil seen above a fibre density of 1.8 g/l, however adsorption trials utilising grease removal, colour and ash content as the indicator showed that
wool density does not start to impact on scouring efficiency until a packing density of over 8.3 g/l is reached. High levels of ultrasonic irradiation adsorption caused by high packing densities are still effective in producing adequate wool scouring.

The effect of ultrasonic irradiation in the cleaning of knitted and woven wool fabrics under conditions normally experienced in domestic hand washing have been investigated. The use of ultrasonic irradiation during laundering in a static bath reduces the level of felting shrinkage while still maintaining or improving cleaning efficiency. Common stains including tea, coffee, red wine, orange coloured carbonated sugar drink and engine oil are reduced in contamination levels more effectively with ultrasonic irradiation when compared to hand washing. The use of ultrasonic irradiation during laundering will result in either a cleaner item after washing or enable a reduction in the amount of detergent used in the wash bath.

Improvements in fabric cleaning are obtained with no significant impact on fabric properties including fabric strength, colour, Martindale abrasion resistance or ICI pilling propensity. Ultrasonic irradiation during static cleaning under the same conditions as domestic hand washing is an effective way of improving cleaning and reducing the impact on garment appearance.

A detailed analysis of individual fibres under high magnification using electron microscope images enables identification of cuticle changes imparted by ultrasonic irradiation. Changes to the fibre cuticle show that irradiation power is proportional to surface damage. Irradiation in the presence of a detergent reduces the surface tension of the fibre liquor interface enabling closer cavitation and higher surface damage. Surface damage is further accelerated by
the presence of an alkali and this may be attributed to a sono-chemical induced increase in the rate of alkali attack of disulphide bonds within the fibre cuticle.

Single fibre measurements have shown that despite some visible changes to the cuticle, ultrasonic irradiation at a fixed frequency range and fixed intensity has a negligible effect on the bending abrasion resistance, tenacity and strain to break of wool fibres scoured in acidic, neutral and alkaline scour liquors.

Fibre cuticle changes provide a difference in the migration path for dyes into the cortex of a wool fibre. Cracking of the fibre cuticle contributes to an increase in dyeing rate when dyeing is undertaken with the pre-metallised dye. Fibre cracking is caused by ultrasonic implosions close to the fibre surface and is directly influenced by treatment power and chemicals present within the treatment liquor. Dyeing rate increases are proportional to the level of cracking on the surface with fibres ultrasonically irradiated in water only showing lower levels of dye exhaustion rate improvement when compared to fibres irradiated in the presence of a detergent and alkali.

Cuticle cracking by ultrasonic pre-treatment in water only provides a small component of the overall improvement in dye exhaustion during isothermal dyeing at 55°C with a contribution of 11-23% depending on the duration of the dyeing. This improvement in the rate of wool dyeing caused by fibre surface cracks is a mechanism of rate increase not previously discussed in publications on ultrasound assisted dyeing. Significant care needs to be taken to ensure that samples have the correct level of degassing and are consistently placed in the same place within the treatment bath otherwise repeatability is significantly compromised.
The use of ultrasonic irradiation for the cleaning of wool is a viable alternative to current technologies as it has the same contaminant removal ability with less fibre entanglement and minimal fibre damage.

6.2 Future Work
This work has investigated the ultrasonic cleaning of wool at one fixed frequency of 40 kHz. In order to further the work a number of key experiments need to be undertaken. These may include the following:

- Investigation on the effect that irradiation frequency has on ultrasonic cleaning. There are conflicting results published about the optimum frequency to undertake detailed cleaning work with low, high and a combination of both recommended. A detailed analysis of the effects of cleaning frequency on contaminant removal for both wool scouring and fabric cleaning would verify the effect that frequency has on contamination removal.

- The effect of fibre wetting has proven to be important in the process of ultrasonic cleaning. Further investigations need to be undertaken to quantify the effect of fibre wetting and liquor dissolved gas levels have on fibre cleaning.

- Investigations into the effect that irradiation frequency has on cuticle surface modifications. This research shows that 20 kHz and 40 kHz ultrasonic irradiation cause fibre cuticle changes, however the work does not compare similar power levels with similar residence times. It is possible that surface modification could be dependent on frequency and this should be investigated.
• Ultrasonic irradiation of the greasy wool scouring liquors has been shown to provide high emulsification of the wool grease. Research needs to be undertaken to ensure that lanolin can still be recovered from the scouring liquor, using centrifuge, at the same rate as from conventional scouring liquors.

• Work needs to be undertaken to determine if fibre cracking results in higher levels of staining after ultrasonic washing.

• Industrial trials need to be carried out on a conventional wool scouring line to ensure that even transmission of ultrasonic irradiation can be achieved throughout the entire scouring bath and that fibre scoured in this method has no effect on downstream processing (carding, top making, spinning, weaving and knitting)
Bibliography


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