SOME CHEMISTRY OF THE WOOL INDUSTRY SCOURING AND YARN PRODUCTION

Wool is one of the two naturally occuring raw materials used world-wide on a huge scale in the textile industry, and has been one of the main earners of foreign exchange for this country. Before export the wool goes through a scouring process - it is washed with detergent to remove dirt and grease.

The role of the Wool Research Organisation of New Zealand, WRONZ, is to find ways of changing wool so it becomes an even more versatile substance and developing new or improved technologies, thus adding value to wool clip.

Wool is a protein, and in the simplest terms consists of a chain of amino-acids residues joined together by amide linkages in the form of an α-helix. The side-chain R groups control the properties of the protein, and a good understanding of wool structure is essential if one is to attempt to modify its properties

This article outlines the structure of wool and describes work in two areas where WRONZ has developed successful new technologies - wool scouring and wet yarn processing.

INTRODUCTION

For many centuries people have exploited the characteristics of the wool fibre. Most know the value of woollen clothing for keeping warm and that it retains this feature even when wet. In the home woollen blankets, carpets and materials all make life more comfortable. Sheepskin rugs are widely used on beds for long term patients to help prevent bed sores, and sheep skin car seat covers are very popular. Sheepskin rugs are a major item tourists to New Zealand buy.

For well over 100 years exports of wool have been a mainstay of the New Zealand economy. Wool was baled in the shearing sheds of the farms and sheepstations and sent overseas by ship. Even today (1996-97) only 13% of the clip is processed beyond the scouring stage in New Zealand.

Despite its long history of use it is only relatively recently that science has unraveled nature's secrets about the molecular structure of wool and allowed us to understand the reasons for its unique properties. The explosion in the development of synthetic fibres in the last fifty years has provided strong competition for wool, and thus it is in the interests of New Zealand for us to find ways of modifying wool's properties to match or improve on those of the new materials, and ways of combining wool with synthetics to produce materials of even more desirable properties.

New Zealand's role in the global wool industry is predominantly as a supplier of well-specified high quality scoured wool blends to the world's textile processors. The creation of added value for this export product by, for example, branding, specification, quality standards, and the addition of special performance features (insect-resistance, etc.) is a crucial part of the industry's commercial strategy.

Although only 13% of the wool clip is processed beyond the scouring stage in New Zealand, several sectors of the wool industry are important as they add value to the primary product and provide jobs. These benefits are demonstrated by the wool scouring industry and the carpet yarn industry. This article discusses some of the chemistry related to these two industries, citing developments made by the Wool Research Organisation of New Zealand (WRONZ).

Textile Chemistry - A Special Discipline

Wool is a major raw material for the textile industry. A textile is defined as a material which has ben fabricated from a fibre asembly. Most chemists working in the textile industry in New Zealand have been trained within normal university chemistry courses. However, textile chemistry is a sufficiently specialised science to have warranted the establishment around the world of a number of dedicated university courses. Departments of colour science and colour chemistry, concentrating on dyeing and related matters, have also been set up. Many of these schools have acquired a highly respected status in the scientific world. Unfortunately there has been a decline of such specialised establishments in recent years, probably due to the relative decline in importance of the textile industry in advanced economies, as textile production has shifted to low-cost and developing countries.

To give some idea of the scope of textile chemistry and the key sub-disciplines, the main areas involved are indicated below.

1. *Aspects of polymer science*
- relating physical properties of fibres to structure and chemical composition
- the chemistry of fibre-forming polymers including proteins (wool, silk) and polysaccharides (cotton, viscose), modifications of polymer and fibre structure, polymeric fibre finishes.

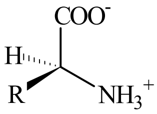
2. *Aspects of surface science*
- physical and chemical properties of fibre surfaces;
- special surface finishes on fibres;
- stability and chemistry of disperse systems (emulsions, foams, latices, etc.);
- wetting and detergency (scouring, cleaning, soiling).

3. *Colour science*
- colour chemistry - dyeing and related technology;
- colour physics - measurement of colour and appearance, including soiling, surface texture, etc.

4. *Analytical chemistry*
- the importance of sound analytical chemistry in all the above areas and others cannot be over-emphasised;
- especially relevant to environmental chemistry (toxic chemical residues, etc.).

STRUCTURE OF WOOL

Wool in its simplest terms is a fibrous protein. Proteins are polymeric substances with relative molecular masses of many thousands. The building blocks of proteins are about twenty aminoacids all but one of which have the formula $^{+}NH_3$-CHR-CO_2^-, and all of which have the same stereochemistry around the chiral carbon atom as shown. (Note that two aminoacids have additional chiral carbons in their ride chains, R.) When the amino group of one molecule condenses with the carboxylic acid group of second molecule to form an amide, (or peptide) link, a dipeptide is formed, $^{+}NH_3$-CHR-CO-NH-CHR-CO_2^-. Condensation with a further aminoacid gives a tripeptide, and the process continues to form a polypeptide. With twenty different R groups the polypeptide can be likened to a string of coloured beads, each different coloured bead representing an aminoacid "residue" with a different R group. The nature and position of the R groups give the protein its unique properties.



Wool in reality is a complex biological structure, composed of an assemblage of cells of differing types held together by modified cell membranes and containing proteins of three major types.

Although in much early wool chemistry, for reasons of simplicity, the biological structure and diverse composition of the fibre was overlooked, modern wool chemists must constantly relate wool chemistry to the biological processes of fibre formation. Thus wool fibre research embraces significant areas of cell biology and molecular genetics as well as classical chemistry.

Some elementary ideas of the complexity of fibre structure can be gained from **Figure 1** and the micrographs of **Figure 2**. Obviously relating fibre properties to chemical structure must involve an understanding of chemistry and structure at a number of different levels of organisation.

In what follows we shall concentrate on the protein components of the cortical cells, which make up the greater part of the fibre. These cell contain three main classes of protein, which may be briefly described as follows.

Intermediate filament (IF) proteins

These are proteins which are 'fibrillar' in that they consist largely of rod-like assemblages of α-helices, but also have end regions which are more globular or random-coil in configuration. The fibrillar IF proteins are aggregrated into complex rod-like structures about 10 nm in diameter which are known as the 'intermediate filaments' (or microfibrils). These in turn are aggregrated into much larger structures within the cell, called macrofibrils. The structure of macrofibrils varies betwen the two main types of cortical cell, ortho- and para-cortex.

Figure 3 illustrates the structure of intermediate filament proteins at the simplest level of organisation, a 2-strand 'coiled-coil' of α-helices, interdispersed with non-helical linker regions.

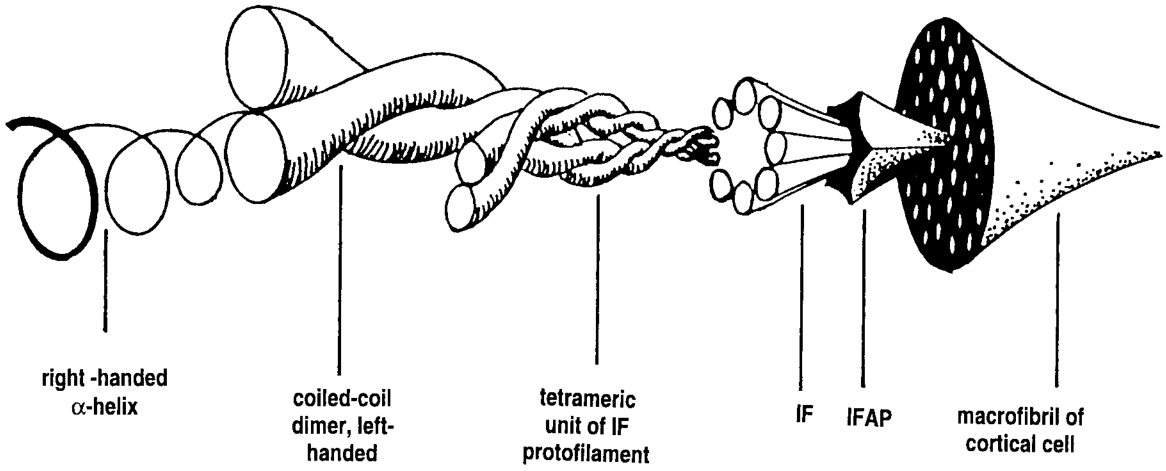


Figure 1 - **'Exploded' diagram of fibre structure from α-helix to macrofibril. The assembly of the tetrameric rod units into the intermediate filament (IF) is complex. The high sulphur matrix proteins are shown here as IFAP, intermediate filamnmt associated protein.**

Intermediate filament proteins typically have molecular masses in the region of 45-50 kDa (relative molecular masses of 45 000 - 50 000). Great advances in th understanding of wool and other tissues occurred in the 1980s when it was realised that the 'microfibrils' in wool and the 'intermediate filaments' of many other filamentous or membranous tissues were almost identical, and essentially the sam structures. This produced an intense cross-fertilisation between wool research and biomedical research in areas such as skin and related tisues. New Zealand was very much in the forefront of this - Professor David Parry of Massey Univesity was (and remains) a world leader in these advances.

Intermediate-filament associated proteins (IFAPs)

This rather of clumsy piece modern jargon refers to the proteins long described in wool research as 'matrix' proteins, because they form a less-organised non-directional matrix in which the rods are embedded. (The analogy of reinforcing rods in concrete is sometimes used.) These proteins are characteristically very high in sulphur (as many as 25% of the amino-acid residues may be half-cystine), and relatively low im molecular mass (10-30 kDa). They are very numerous, and somewhat variable in relative amount depending on nutrition, etc.

Matrix proteins, by virtue of their high content of cystine, are usually credited with being responsible for the disulphide bond crosslinking which gives the fibre its mechanical and chemical integrity. In fact very little is known about the conformatiom of matrix proteins, or the pattern of crosslinking involving half-cystine residues. Very recent studies of model peptides based on matrix protein fragments strongly suggest that almost all the disulphide

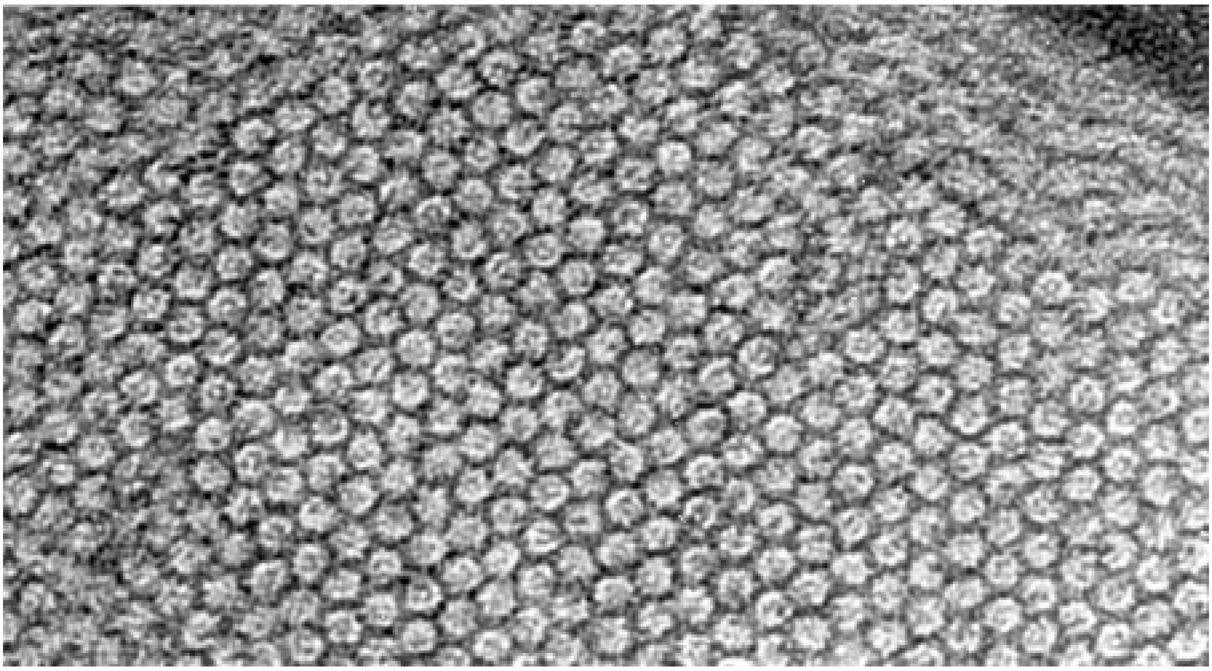


Figure 2(a) - **Electron micrograph of a transverse section of part of a cortical cell (mesocortex) showing the close-packed hexagonal array of intermediate filaments, sufounded by densely stained 'matrix' of IFAP high sulphur proteins. Magnification = 736 000 x. The separation of intermediate filaments is about 8.6 nm.**

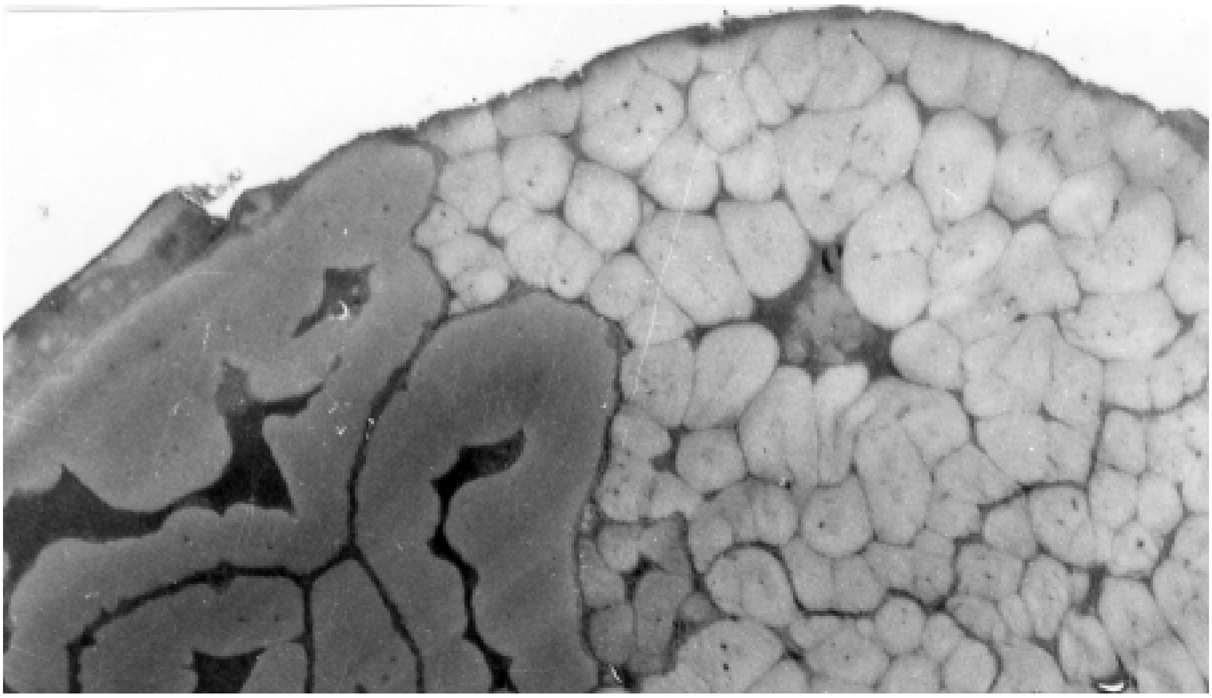


Figure 2(b) - **Electron micrograph of a transverse section of a wool fibre, showing lightly stained, differentiated macrofibrils in the orthocortex, and densely stained, fused macrofibrils in the paracortex. Note also the cell boundary structures. The dark zones, particularly in the paracortex, are regions of non-keratinous cytoplasmic remnants. Magnification = 25 000 x. (Micrographs courtesy of J L Woods, WRONZ)**

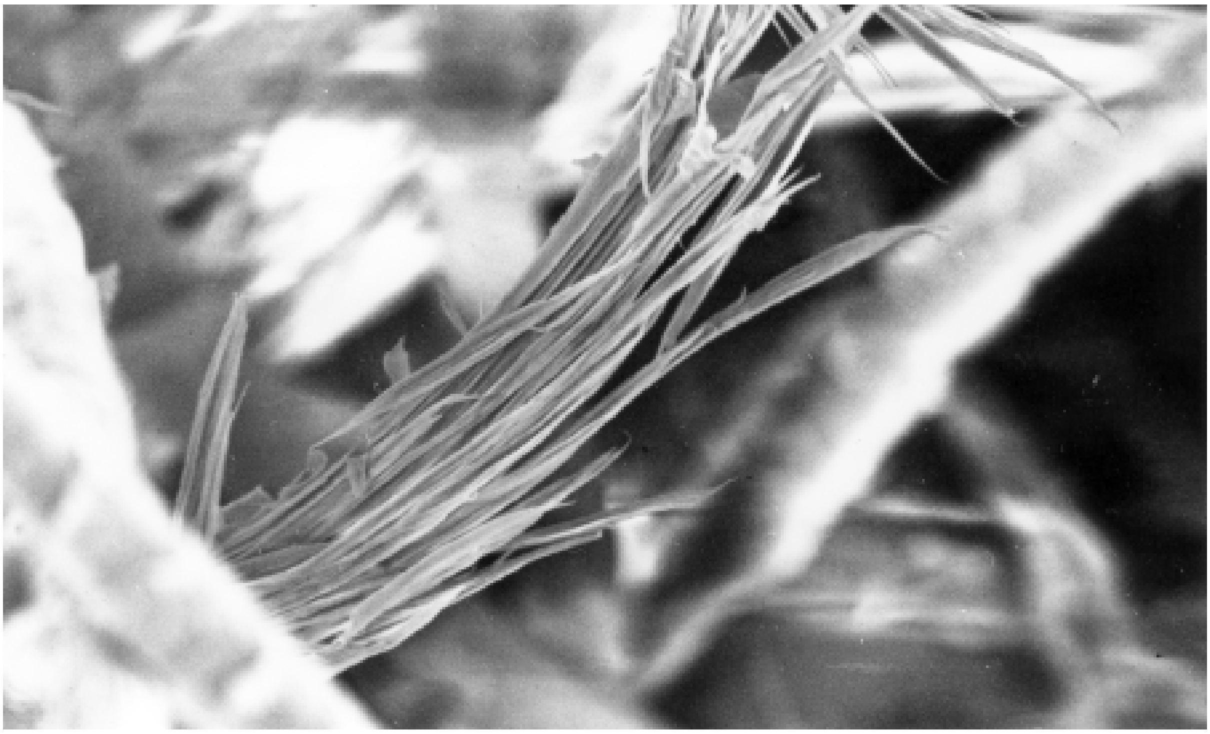


Figure 2(c) - Scanning electron micrograph of a severly mechanically disrupted fibre (ina carpet tuft), clearly showing the disintegration into cortical cells. Magnification = 800 x.

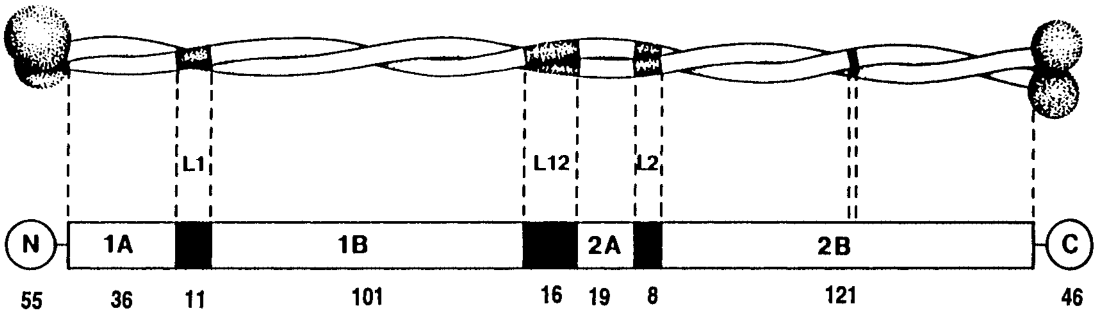


Figure 3 - Schematic model of a coiled-coil dimer, showing the helical rod-like segments 1A, 1B, 2A, 2B, and the non-helical linker segments. The two protein chains run parallel and are different in amino-acid composition. The numbers below each segment are the numbers or amino-acid segments in each chain in the segements for a typical wool IF prorein. The overall length of the rod domain (1A→2B) is 47 nm. The balls on the end represent he non-helical tails of the IF proteins, the exact conformation and arrangement of which is not clear.

bonds in these proteins are intramolecular, between near neighbours, to form rings closed with disulphide bonds. The long-range crosslinking is probably formed between a small number of the matrix cystine residues, and the relatively few cystines present in the IFs and their globular tails. This is consistent with inferences from applied science and technology.

High tyrosine-glycine (HGT) proteins

These proteins rich, in the amino-acids tyrosine and glycine, form a relatively minor third class of proteins. Their occurrence is restricted to certain parts of the fibre. They are relatively low in molecular mass. Their function is not clearly understood and we ned not deal with them further here.

Helix structure

The proposal of the α-helix structure of polypeptides by the famous double Nobel-laureate Linus Pauling and his colleagues in 1951 was one of the great breakthroughs of protein research. In this model structure, there is a 'residue transition' (ie. the axial distance traversed by each by each aminoacid residue) of approximately 0.15 nm. This was consistent with key results from early X-ray diffraction work on filamentous α-keratin.

The structure is stabilised by intra-chain hydrogen bonds involving the hydrogen on the -NH group of one residue and the oxygen of the amide bond three further residues along the chain. In the classical α-helix structure, there are 3.6 aminoacid residues per turn, or 18 residues in 5 turns, over an axial length of 2.7 nm (0.15 nm/residue).

In natural proteins, all the aminoacids have the L-configuration and the α-helix is invariably right-handed, ie. if you were to slide down it you would always be tuening to the right. (However this is not necessarily the case in all synthetic polypeptides.) When two chains coil around one-another to form a coiled-coil, the twist of the coiled coil, as seen in **Figure 3**, is left handed. In the coiled-coil, the two protein chains are in the same sense (parallel rather than anti-parallel).

It is useful to understand what the word 'helix' really means. Books such as the well known 'Double Helix', relating to the exciting story of the elucidation of DNA structure by Watson and Crick, have perhaps helped fuel popular misconception that there is something 'biological' about 'helix' molecules.

In fact, the term helical means nothing more than that the molecule rpeats itself periodically in the axial direction. Well-ordered synthetic polymers form structures which are every bit as helical as those of proteins or DNA.

The words 'crystalline' and 'amorphous' have often been used in the past to describe the fibrillar and matrix regions of the fibre. These terms have been deliberately avoided, as neither is accurate. The structures present in the fibre demonstrate that there are many forms of structural organisation between thetruely crystalline and amorphous.

Relationship of structure to mechanical properties

The mechanical associatin via cross-linking between the filaments and the matrix is largely responsible for the observed mechanical properties of the fibre. An on-going goal of academic wool fibe physicists is to develop a model of mechanical behaviour which accurately reproduces the observed mechanical behaviour (both in tension and in relaxtion, see **Figure 5**).

A diagram of one relavent mechanical model, showing coupling between the filaments and the matrix is given in **Figure 4**.

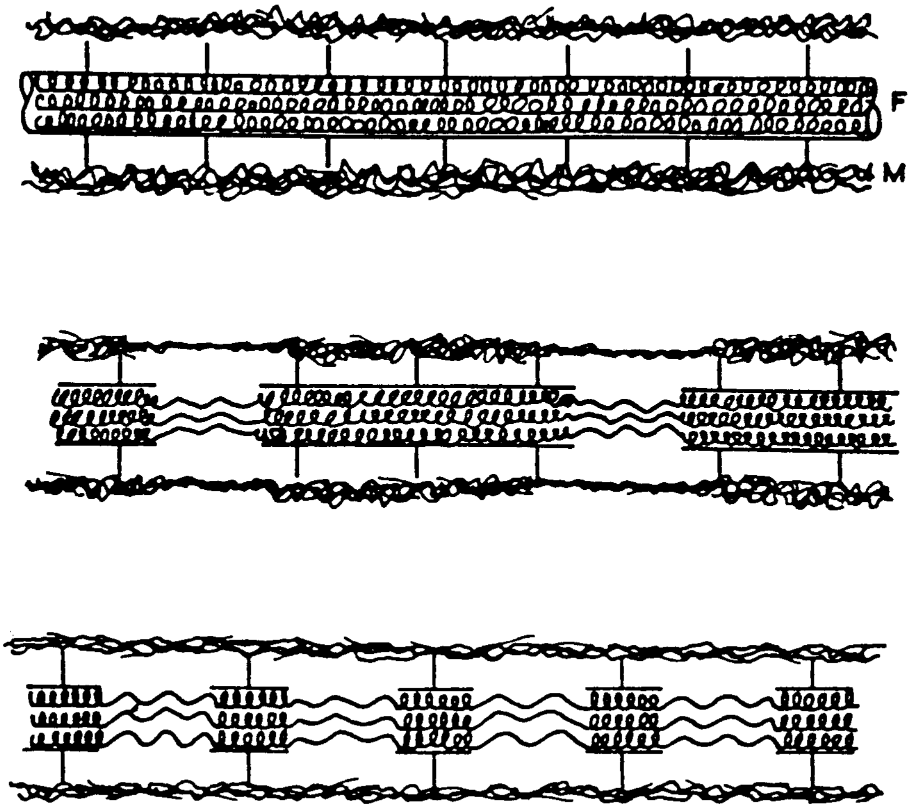


Figure 4 - **A model of a wool fibre structure showing the fibril (F, top) and martix (M,top) regions with periodic linkages between fibrils and matrix. Top: the unstretched state. Middle and lower: two successive stages of stretching, in which regions of the α-helices are unfolding into β-pleated sheets, with stretching of the associated regions of matrix. (This model, though proposed in 1969, in consistent with much modern structural information.**

Wool has a unique form of strain-stress curve, depicted in **Figure 5**. One of the key features is the flat yield region where the fibre extends at constant stress. It has ben shown that this mechanical feature is associated with conversion of α-helical rods to extended-chain structures known as β-pleated sheets (which are also strongly hydrogen-bonded). The α□β conversion is an important feature of wool behaviour. At the same time as the helices are extended the matrix is als stretched. Recovery of the fibre when the stress is released is assisted by the retractive force of the strained disulphide bond network, much like a rubber. In fact, as seen later in this article, there is a lot in common between wool and the polysulphide rubbers in mechanical behaviour.

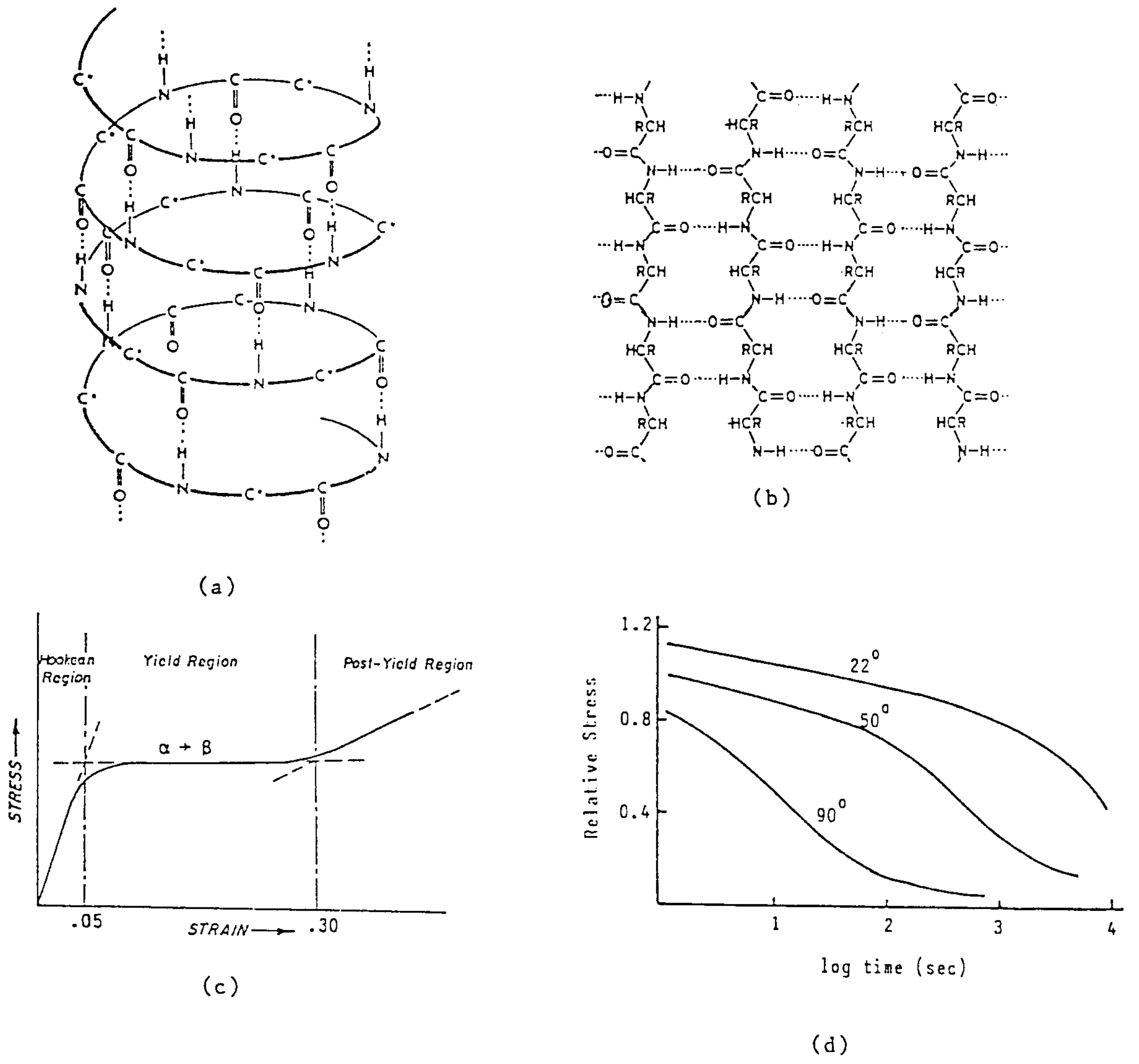


Figure 5 - Aspects of structure and mechanical properties of wool
(a) a schematic representation of α-helix structure, stabilised by intra-molecular hydrogen bonds, as adopted by fibrillar proteins of the unstrained fibre.
(b) β-pleated sheet structure, stabilised by inter-molecular hydrogn bonds, as adopted by zones of the fibrils when the fibre is stretched to the end of the yield region.
(c) stress-strain diagram for wool fibre, showing yield region associated with α→β transformation.
(d) stress-decay curves (relative stress vs log *time*) for wool fibres at 40% strain, in pH 7 buffer, at various temperatures (the rate of stress decay is closely related to the rate of the thiol-disulphide interchange reaction - see following section on wool yarn setting).

Surrounding the cortical cells are protective layers of scales. It is often the case that nature has perfected a masterpiece of engineering design which man can merely copy. The design of the wool fibre is copied in high class climbing ropes which are coiled bundles which are in turn coiled, and the whole structure surrounded in a protective sheath.

WOOL SCOURING

Wool as shorn from the sheep is known as greasy (or raw) wool. Before it is suitable for further processing it must be washed to remove dirt, water soluble contaminants (called suint), and woolgrease. This process is known as scouring.

The wool scouring industry currently scours about 80% of the country's wool clip, adding value in the process of some $50 M. The industry developed rapidly through the ‘70s and ‘80s and achieved a position of world leadership. This growth was based on technology developed by WRONZ in conjunction with the woolscouring industry and equipment manufacturers.

The very large improvements in productivity which have resulted have caused concentration of the industry into a much smaller number of plants (14 in 1998, compared with 26 in 1989).

Figure 6 shows a rather simplified diagram of a typical conventional 6-bowl wool scour.

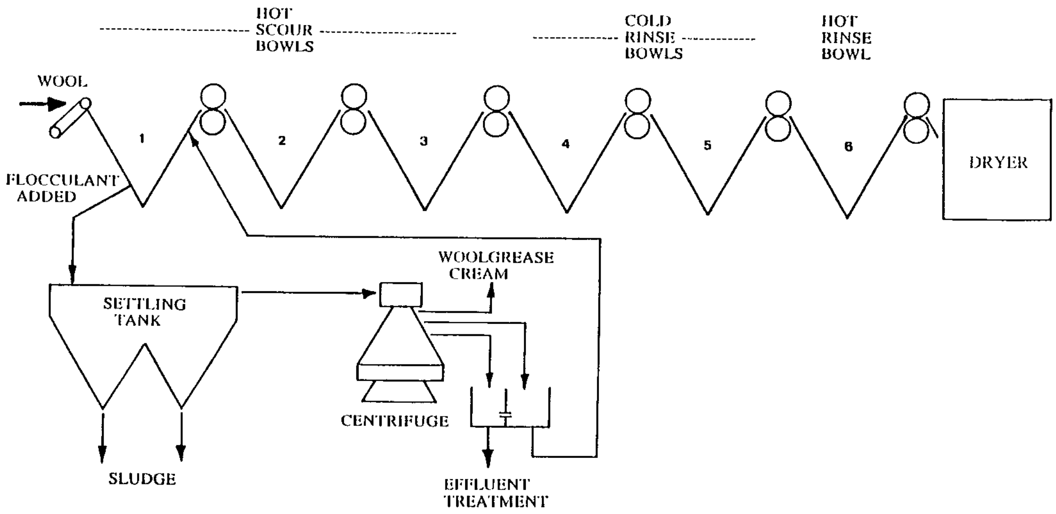


Figure 6 - **Simplified layout of a typical commercial woolscouring plant showing liquor treatment loop for dirt and grease removal. The latest plants have 8 bowls, sophisticated control systems, multiple centrifuges, and liquor handling loops which are much more detailed than shown in the diagram.**

The wool passes through a series of bowls, each separated from the next by large pressurised squeeze rollers. There are (usually) six bowls; the first three are scouring bowls and contain hot detergent solution, (about 60°C, 1-3 g/L); the next two bowls are cold rinse bowls; and the final bowl is a hot (60°C) rinse. The squeeze rollers minimise the carry over of contamination from one bowl to the next, and this is assisted by a general flow of the hot liquors against the direction of the wool flow. Liquor from the first (most contaminated) bowl is cycled through dirt and woolgrease removal equipment, after which some, about 1 litre/kg greasy wool, is run to drain. This loss of liquor from bowl 1 is made up with liquor from bowl 2, and so on. The amount of wool a single scour train can process depends on the width of the train; the range is from 0.6-5 tonnes of greasy wool per hour. The wool passes through the whole plant (scouring, drying, and baling) in about 20-30 minutes.

The following notes relate to some aspects of scouring chemistry relevant to modern activities. Some further aspects of interesting chemistry relating to the industry are described in early editions of 'Chemical Processes in New Zealand'.

Contaminants in Wool

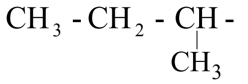
Raw wool contains three main contaminants, woolgrease, suint, and dirt, which combined make up some 20-30% of the fleece weight. A typical figure of the grease content of crossbred wool is about 6%.

- *Woolgrease*

This is a very complex mixture, consisting mostly of esters of various long-chain fatty acids with long-chain alcohols and sterols. Technically it is a wax, rather than a fat, because glycerol esters are not present.

The fatty acids present fall into four main classes.

- a normal paraffin series, with even carbon numbers approximately from C_{10} to C_{26}.
- an *iso*-acid series, with the alkyl chain terminating in a $(CH_3)_2$-CH- group, with even carbon numbers from C_{10} to C_{28}.
- an *anteiso*-acid series, with a terminal *iso*butyl group, ie,



$$CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-$$

  with <u>odd</u> numbers of carbons from C_9 to C_{31}.

- α-hydroxy normal and iso- acids, ie, R-CH(OH)-COOH with even carbon numbers from about C_{12} to C_{32}.

The alcohols are even more complex. There are aliphatic alcohols corresponding to the same series of structures as the acids, ie

- normal alcohols from C_{18} to C_{30}
- *iso*-alcohols from C_{18} to C_{26}
- *anteiso*-alcohols from C_{17} to C_{27}
- 1,2-diols, ie, R-CH(OH)-CH_2OH, both normal and iso, C_{16} to C_{24}.

However, the major part of the alcohol fraction consists of sterols; the most important member is cholesterol, followed by lanosterol and dihydrolanosterol. Smaller amounts of other sterol derivatives are present.

Clearly the esters formed from these acids and alcohols form a bewildering variety, especially when one considers that the hydroxy-acids and the diols can form di-esters.

In addition to the esters, free fatty acids are present, along with other 'impurities' such as soaps (metal salts of fatty acids). Calcium soaps are particularly important. These arise mainly from the fellmongery production of slipe wool with lime-sulphide depilatories, and can cause problems in the centrifugal separation of woolgrease as well as in woolgrease refining.

Refined woolgrease is known as lanolin, which is the product resulting from deodorisation, decolorisation, neutralisation and removal of entrained water ('volatiles'). Lanolin is an important item of commerce. However, the most sought-after product from woolgrease is the mixed 'wool-wax alcohols'. These are produced by hydrolysis (saponification, or 'soap-making') of the esters followed by solvent extraction of the alcohols. These are widely used in toiletries and medicinal preparations because of their ability to form stable emulsions entraining large amounts of water.

A considerable amount of woolgrease is still used to produce cholesterol, which typically forms about 12-14% by mass of New Zealand crossbred woolgreases. This is recovered in a separate process from wool wax alcohol production.

There are many historical uses of lanolin and derived products, but more sophisticated modern applications are needed especially for the woolgrease acids which are by-products of alcohol manufacture.

- ***Suint***

Suint is the 'sweat' of the sheep and is a complex mixture of water-soluble salts. The predominant cation is potassium; the anions include carbonate, bicarbonate, various low-molecular-weight mono- and di-carboxylic acids (succinic, glycollic, glutaric, etc) and smaller amounts of long chain fatty acid anions which may originate from woolgrease. Peptides and other nitrogenous substances are minor components.

The long-chain suint anions are in themselves surface active and act as effective soil dispersing agents during scouring. In New Zealand greasy crossbred wools the suint pH is usually about 8.5-9.0, so the fatty acids are ionised and act as anionic surfactants (soaps) participating in the stabilisation of the woolgrease emulsion by conferring a negative charge to the emulsion particles.

Consequently, one of the key steps in emulsion destabilisation for effluent treatments is acidification, to convert those soaps to acids, thus destroying their surface charge and facilitating coalescence. This process is known as 'acid cracking'.

There is overlap between components of suint and grease scour liquors when they are analysed by the conventional solvent extraction test. Thus, some of the 'grease' component analysed by extraction of liquor with petroleum ether is also water soluble. The distinction between suint and grease components, especially in oxidised wools, is thus poorly defined.

- ***Dirt***

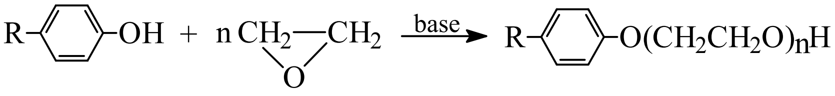
'Dirt' consists of all the ill-defined solid fleece contaminants. It includes mineral soil, wind blown dust, vegetable matter, faecal matter (dags), skin flakes, discarded cuticle cells, and fragments of fibre broken from brittle photo-oxidised tips. In many respects, in terms of wool properties, it is the very fine mineral material, largely associated with exposed fibre tips, that is the most significant.

Detergent Selection

Until the 1960's wool was conventionally washed in an aqueous bath containing soap and alkali (usually sodium carbonate). It was necessary for soft water to be used because of the insolubility of calcium and magnesium soaps. In fact the wool textile industry developed in the Yorkshire area of the UK because of its abundance of soft water. Scouring wool with soap and alkali was a process which had to be undertaken with some care because of the susceptibility of wool to damage by alkali. Therefore it was with some relief that the industry greeted the introduction of synthetic detergents which were unaffected by hard water and were cost effective in degreasing wool. Originally these were anionic and it was found that alkali was still needed to avoid undue loss of detergent by adsorption on to the wool. The later introduction of nonionic detergents removed this constraint, and wool was able to be washed with these detergents alone.

For many years now, scouring in New Zealand has been carried out with nonionic detergents formed by the chain growth polymerisation reaction of ethylene oxide (EO) with an alkylphenolate ion, where the alkyl group is typically a highly branched C_9 chain.

The overall reaction is:



although the reaction is rather more complex than implied by this equation.

These nonylphenol-ethylene oxide condensate detergents may conveniently be described as NPEOX types, where X is a numeral denoting the number of moles of EO in the product. The woolscouring detergent most commonly employed in New Zealand is approximately a NPEO9 type. More recently, primary alcohol ethoxylate detergents have been added to those in regular use in New Zealand. There are two reasons for using these in preference to NPEO types. The first is that residues of NPEO detergents are undesirable in products produced from refined woolgrease. The second is that NPEO detergents are comparatively difficult to biodegrade, and their use may result in the introduction of relatively long-lived and toxic phenolic residues into the environment. Thus wool processors working to an ‘Environmental Choice’ standard will prefer to use comparatively easily biodegraded and non-toxic alcohol ethoxylate products.

Unfortunately, alcohol ethoxylate detergents which best address the needs of woolgrease refiners are not the best for woolscouring. If grease properties are paramount, detergents of the general type of

$$CH_3\,(CH_2)_{7\text{–}9}\,CH_2\text{ - }O\,(CH_2CH_2O)_6\,H,$$

may be used, while for best woolscouring molecules with larger hydrophobes and longer EO chains are preferred, for example

$$CH_3\,(CH_2)_{10\text{–}13}\,CH_2O\,(CH_2CH_2O)_9\,H$$

If the hydrophobe is linear, the biodegradability is also enhanced.

The detergent molecules contain a hydrophobic part which is the hydrocarbon ‘moiety’ and a hydrophilic portion formed of the polyoxyethylene chain. Thus when woolgrease, a hydrophobic substance, is removed from the fibre surface by detergent action, a stable grease micelle is formed in which the hydrocarbon moiety is embedded in the emulsified grease, while the hydrophilic polyoxyethylene chain mingles with the surrounding water. As mentioned previously anionic compounds from the woolgrease and suint (fatty acid anions) also act as surface active agents and assist in stabilising the woolgrease dispersion. Dirt particles (largely mineral) are also entrained in and emulsified with the grease. Soluble proteins, absorbed onto or interacting with the droplet surface, add to the complexity of the structures. The result of this process of grease emulsification (which takes place mostly at about 60□C, above the woolgrease melting temperature) is an extremely stable dispersion of woolgrease and dirt which defies most conventional methods of demulsification and phase separation. This dispersion stability greatly complicates issues of effluent treatment.

Dispersed particles in the liquor exist in two size ranges. The larger diameter particles (2-12 µm diameter) may be largely separated from the aqueous medium by centrifugation, leading to the recovery of woolgrease as a by-product of scouring. This opens up a separate topic rich in chemistry, the recovery, purification, and saponification (hydrolysis) of woolgrease.

Characterisation of Detergents

WRONZ has carried out many investigations on detergent composition and efficiency. With respect to the nonionic detergents used in woolscouring and yarn processing (see next section) the following are some of the key molecular characteristics which determine the efficiency of these detergents.

1. Structure of the hydrophobe

In alkylphenol ethoxylates, the alkyl substituent typically consists of a C_9 chain, which is capable of having many isomeric forms (**Figure 7**).

It is possible to determine the relative amounts of the different classes of structures shown using the technique of ^{13}C nuclear magnetic resonance spectroscopy.

The most common product manufactured has C_9 substituents produced by the condensation of three moles of propylene, leading to the highly branched structures at the bottom of the figure. As such products are well tested by experience, they are preferred as wool scouring detergents (setting aside biodegradability issues).

2. Ethylene oxide chain length and distribution

The average number of moles of ethylene oxide per mole of hydrophobe should be (for raw wool scouring) between 9 and 10 (64-67% by mass EO in the product). However, the distribution of ethylene oxide numbers is also very important - it is not permissible to mix two products of high and low EO numbers for example. As a result of the mechanism of the ethoxylation reaction, with its stepwise addition of EO units, the distribution of ethylene oxide numbers in the product follows a Poisson probability distribution (this is essentially a distribution resulting from the probability of some integral number of events, in this case additions of EO units at a particular site, ie, the original alkylphenoxide ion, occurring over the duration of the reaction time).

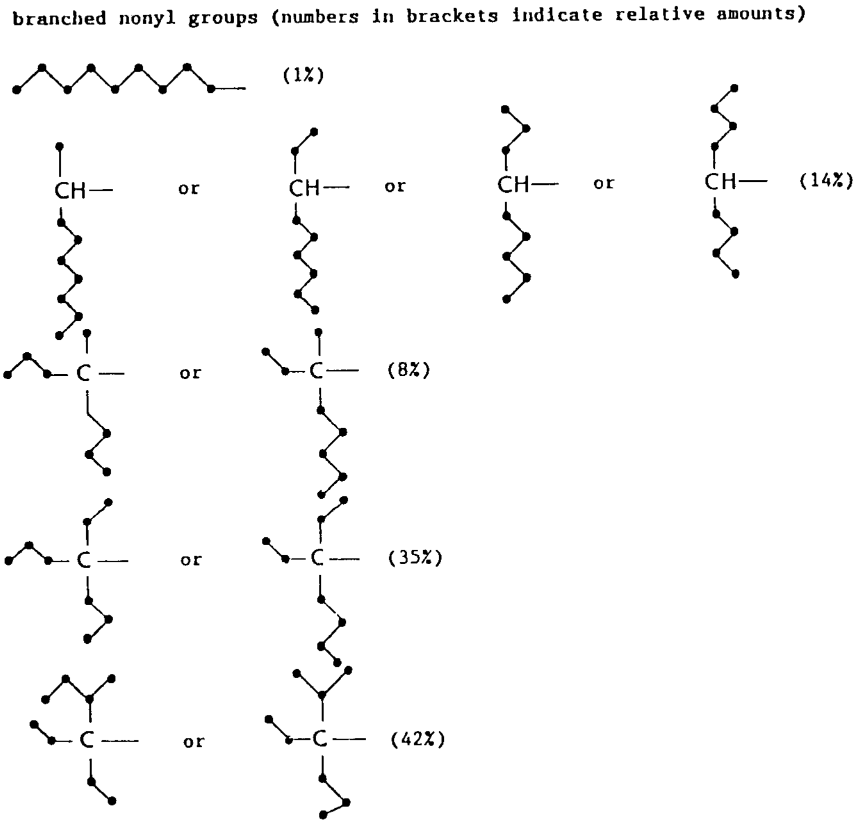


Figure 7 - **Diagrams showing various patterns of the nonyl groups in nonylphenol ethoxylate surfactants. The bottom isomers, created from combination of propylene molecules, give the most preferred hydrophobes for woolscouring efficiency.**

Figure 8 shows a preferred Poisson distribution of EO numbers in an alkylphenol ethoxylate, as well as a different bimodal distribution created by mixing products, which would be very likely to be inadequate in emulsifying power, foaming characteristics, etc.

Mass spectroscopy is a very enlightening technique to apply to detergent structure. Using a technique known as fast atom bombardment, with the target molecule (ethoxylated product) embedded in a complex matrix containing potassium salts, it is possible to charge and eject from the target ions of the ethoxylated product complexed with potassium. A simple example of the resultant mass spectrum is shown in **Figure 9**. This is for an alcohol ethoxylate with a single C_{13} hydrophobe. Note the major mass peaks differing by 44 mass units (ie, a -CH_2CH_2O- unit), and the approximately Poisson-like distribution.

When the hydrophobe is also complex, a number of similar patterns reflecting the mass distribution in the hydrophobe are overlaid. However, by a combination of ^{13}C magnetic resonance, mass spectroscopy, and high performance liquid chromatography (to separate and visualise the different molecular species), such complex products may be ‘taken apart’, and their composition understood in detail.

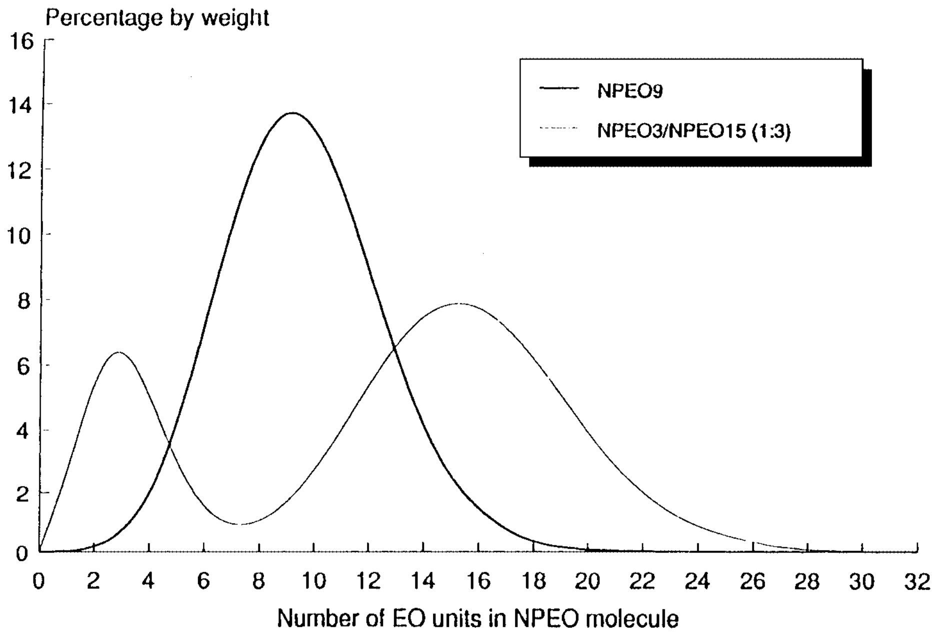


Figure 8 - **Distribution of number of EO units in a normal NPEO9 surfactant, and in another (hypothetical) mixed product also averaging 9 EO units per molecule. The former curve follows a Poisson distribution arising from the anionic polymerisation reaction.**

Liquor Processing and Woolgrease Recovery

As indicated in the scour diagram (**Figure 6**), heavily contaminated liquor from bowl 1 is continuously recycled through a settling tank (or more commonly now a dirt-removal hydrocyclone) and a centrifuge which removes woolgrease from the liquor.

Removal of the emulsified woolgrease is not simple, as its separation by the centrifugal forces is governed by the equation, derived from Stokes' law,

$$V = \frac{2\omega^2 \, xr^2 \, (\rho - \rho')}{9\eta}$$

where V is the velocity of an emulsion droplet at a radial position x in the centrifuge, $\omega^2 x$ is the acceleration acting on the droplet ($\omega^2 x/g$ = number of 'g forces' where g = acceleration due to gravity), (ρ-ρ') = density difference between the droplet and the aqueous medium, r is the radius of the droplet and η is the viscosity of the aqueous medium.

While woolgrease itself has a significant density different from its aqueous environment, the inclusion of microscopic dirt components in the grease decreases the density difference, so that often only very small density differences are available to effect separation. Moreover, as mentioned above, many of the grease emulsion droplets are very small, □ 1 µm in size, and therefore very difficult to separate. It is only the larger particles in the bimodal distribution (see **Figure 10**) which are able to be centrifugally recovered. It has been clearly shown that the grease in those larger particles originates from the butt of the staple where the woolgrease has undergone less environmental degradation. Woolgrease in liquors is often divided into 'oxidised' and 'unoxidised' categories, although the precise meaning of these terms is vague.

‘Unoxidised’ grease is mostly unmodified wax esters as secreted into the fleece, whereas ‘oxidised’ grease contains more polar components such as fatty acids, hydroxy-acids, and keto-acids, and other components arising from environmental degradation on the fleece. Because of the open fleece structure of New Zealand crossbred sheep, New Zealand woolgrease is more ‘oxidised’; so New Zealand woolgrease recovery rates are relatively low, compared to the Merino-based industry in Australia. Typically only about 30% of grease in the fleece is recovered in New Zealand, the rest being discharged into effluent systems of various sorts, where it imposes a very large pollution load in terms of BOD, with its associated dirt contributing to suspended solids.

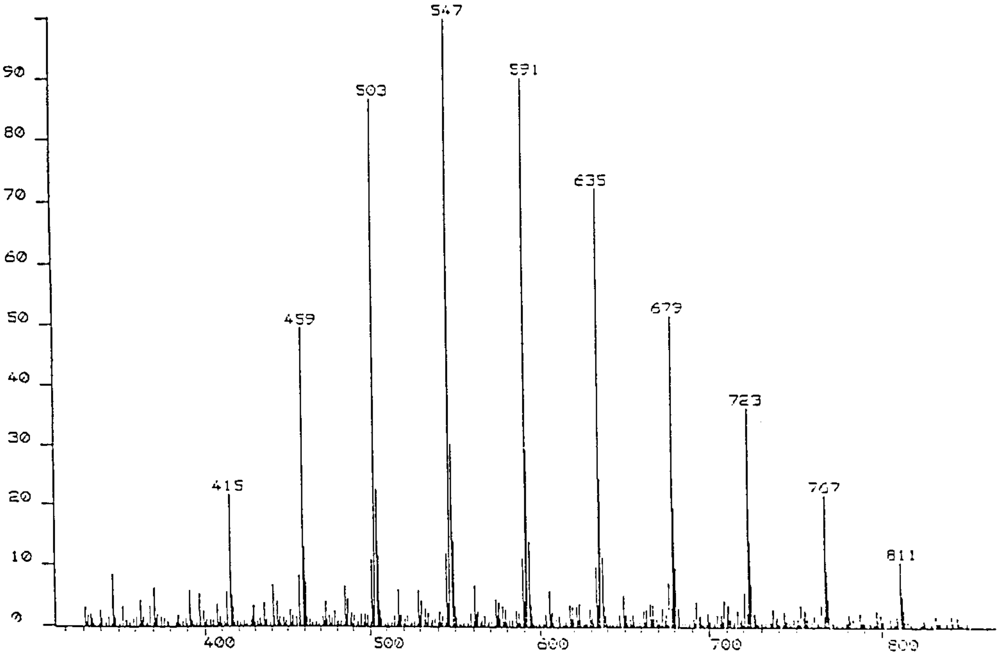


Figure 9 - **FAB-mass spectrum of an alcohol ethoxylate with a single branched hydophobe of molecular formula $C_{13}H_{27}O$-. Major peaks differ by 44 mass units, corresponding to an EO unit. The ions ejected are $C_{13}H_{27}O(EO)_nH.K^+$, ionic mass = 239 + n (44); therefore the 415 peak contains 4 EO units, and so on.**

Woolscour Effluent Characteristics

For the design of effective effluent treatment systems it is necessary to understand the contributions of the various effluent components to the total pollution load as measured by oxygen demand, either BOD (biological oxygen demand) or COD (chemical oxygen demand).

The separation of effluents into grease/dirt fractions and suint solutions during ultrafiltration trials provided an opportunity to develop statistical relationships for BOD and COD loadings in terms of grease, suint, and dirt contents.

The relationships for BOD_5, and COD were found to be

$$BOD_5 = 2{,}400 \times \text{suint} + 5{,}100 \times \text{oxidised grease} + 11{,}350 \times \text{top grease} + 185$$

$$COD = 8{,}267 \times \text{suint} + 30{,}980 \times \text{oxidised grease} + 28{,}236 \times \text{top grease} + 6454 \times \text{dirt} + 1536$$

Here BOD and COD are measured in mg/L, and the contaminants are measured as percentage by mass of the effluent. 'Top grease' is a laboratory measure of recoverable grease which may be roughly regarded as 'oxidised' grease; non-recoverage grease is 'oxidised grease'.

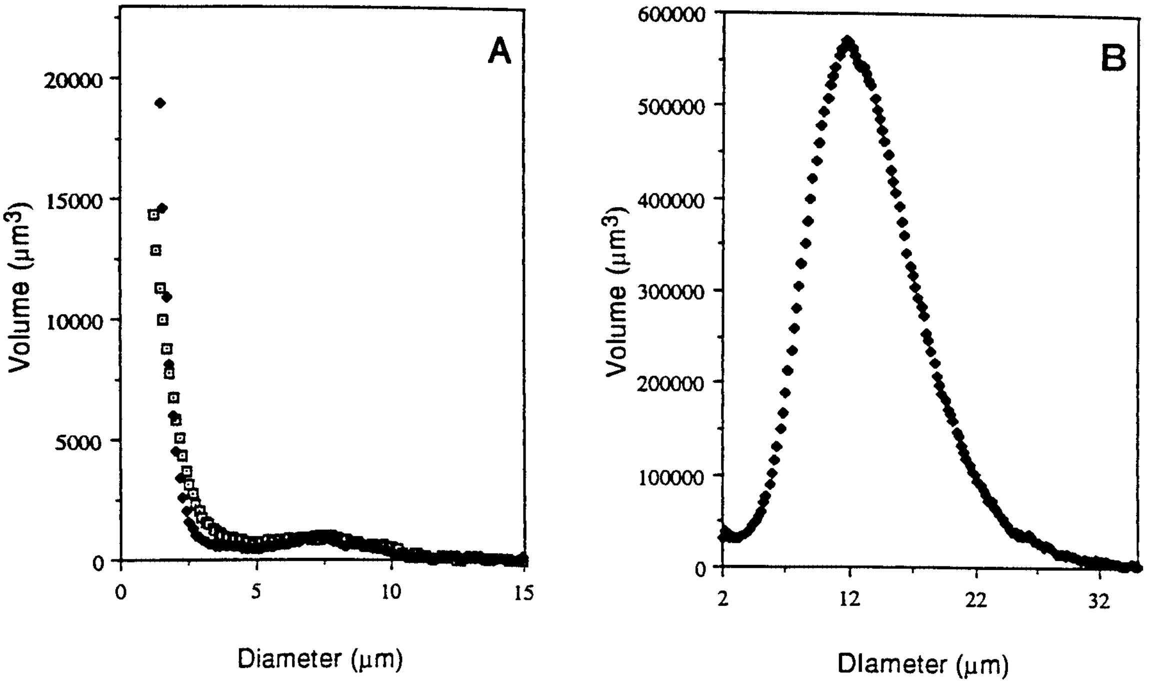


Figure 10 - **Particle size distributions (as measured by Coulter counter) in the liquid feed of a grease-recovery centifuge (left), and in the centrifugally recovered cream (right). During centrifuging, the larger droplets in the small peak centred on about 7.5 µm are preferentially removed and partially coalesced, leading to the emulsion particles centred on about 12 µm in the recovered cream. (In practice this cream is thermally cracked and anhydrous woolgrease recovered in a purifier centrifuge.)**

Figure 11 shows the agreement between measured and calculated COD using the above relationship. The correlation for BOD_5 is slightly poorer due to the vagaries of the experimental method.

These very valuable relationships highlight the desirability of removing grease from discharged effluents as it is the largest contributor to BOD and COD. Continuous improvement in liquor management and grease recovery has reduced the pollution potential of woolscouring markedly.

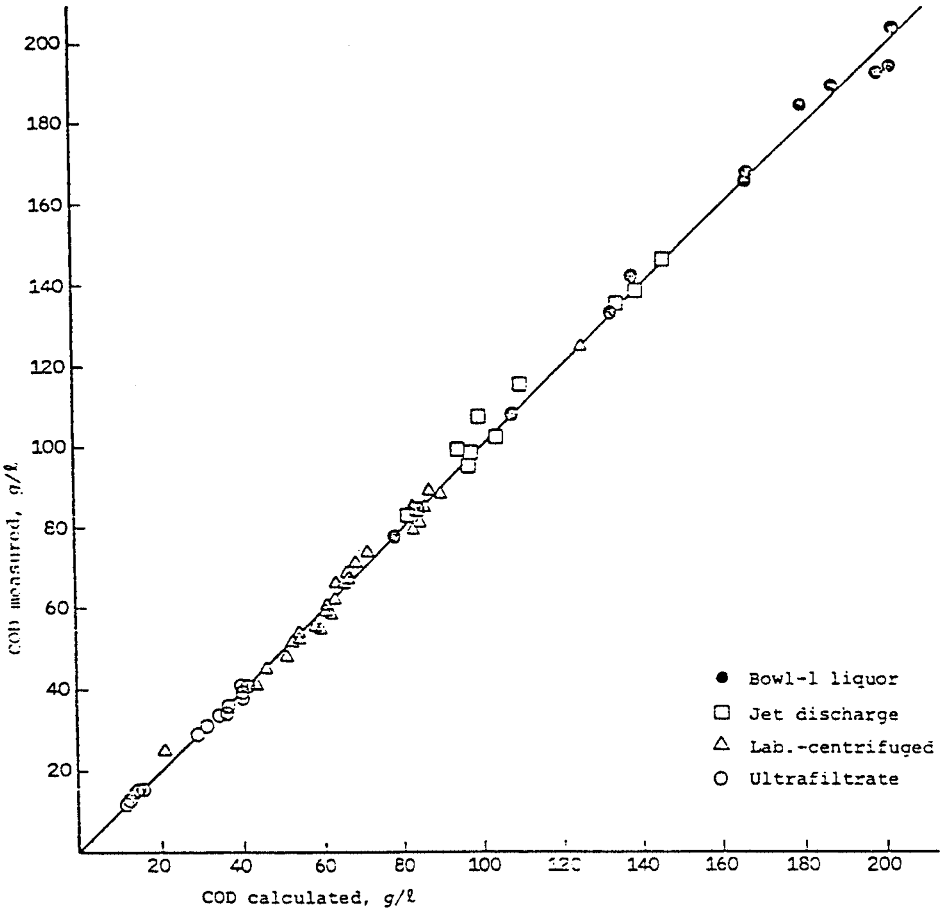


Figure 11 - **Comparison of experimentally measured and predicted COD values in wool scour effluents, using the statistical relationship in the text. Clearly, COD values may be accurately predicted from liquor composition parameters.**

Chemical Aspects of Effluent Treatment

Woolscour effluent treatment has fortunately come a long way since the days when it was a boyish prank to set fire to the canals of Bradford, which generated large quantities of methane from the anaerobic degradation of woolscouring effluents.

A variety of methods of treating woolscour effluents are utilised around the world and in New Zealand. These vary from very capital intensive 'complete' treatments involving evaporation of the flowdown effluent, followed by incineration (or pyrolysis) of the grease-rich solids, to systems of land disposal involving irrigation, wetland treatment, or pelletisation of solid wastes and sludges followed by land spreading or composting.

A number of physico-chemical effluent treatment systems are in use or under development. These are basically flocculation technologies in which the effluent is first acidified and the 'acid-cracking' assisted by the addition of a polyelectrolyte flocculant. These are often of the form of poly(acrylamide) with positively charged ($-NH_3^+$) pendant groups. These cationic polyelectrolytes interact with the still somewhat negatively charged emulsion, precipitating the uncharged complex as a settled floc. The flocculated material can be separated as a high-solids sludge using a decanter centrifuge. The 'supernatant' from the floc is essentially a suint solution, which though still very high in BOD can be relatively easily treated by aerobic treatment, or may in some instances be irrigated onto land or be accepted in an industrial sewer. The heavy sludge may be evaporated, or disposed of to land or composting. Both sludge and supernatant are rich in potassium, and therefore have fertiliser value - indeed the acceptable potassium loading onto land may be the limiting factor in determining the area over which such land disposal may be environmentally sustainable.

The Sirolan CF effluent treatment system developed by CSIRO in Australia is an example of such an acid flocculation treatment system. In New Zealand, WRONZ and ADM Group developed a similar process in which the emulsion destabilisation was effected by short-term anaerobic treatment, followed by a slight flocculant addition. Acid is added later in this process to assist decantation of the floc. A demonstration plant of this type, known as Bioloop□, is in operation at Ashburton Wool Scour.

Membrane separation technologies can achieve similar results in terms of separation of grease and dirt from suint. Overseas there is an increasing trend to cleaning up and recycling comparatively clean rinsewater using membrane filtration techniques, but in New Zealand the costs of such processes are not yet justified.

Additional Chemical Treatments in the Woolscour

- *Bleaching*

A very common process in New Zealand woolscours is the bleaching of wool with hydrogen peroxide. This both improves the brightness and reduces the yellowness of the fibre. Bleaching is carried out in the relatively clean liquors of the final scour bowl, at about 60°C, and traditionally at a pH of 4-5 with formic acid. The use of formic acid is often not necessary and neutral bleaching is increasingly common.

The chemical reactions which bleach the wool are unknown, but they take place in the dryer after application of the peroxide, rather than in the bowl itself. The most obvious chemical effect of bleaching is that a portion of the cystine disulphide bonds are oxidised to cysteic acid, in which the sulphur is present as $-SO_3H$ groups. This impairs the setting chemistry of wool, and if carried to excess can adversely affect mechanical properties and chemical resistance. Therefore bleaching must be carefully controlled and confined to peroxide concentrations of less than about 10 g/L (though scourers still define peroxide in terms of 'volumes'; 1 volume ~ 3 g/L).

- *pH Control*

An increasing amount of wool is now processed in the scour to emerge with a specified pH, usually mildly acid or neutral (remember that its natural pH is mildly alkaline). Because the acid combining power of wool is very large, and its equilibrium absorption very dependent on ionic strength, the accurate control of wool pH in a scour is far from the trivial matter it may appear. However, as a result of research and experience this can now be accurately achieved. The stimulus for this pH modification is that it aids subsequent dyeing, which is carried out under acid conditions. This is especially important for the continuous dyeing of carpets, in which case there is no opportunity before dyeing to reduce the pH of the wool.

- *Product Differentiation*

One of the problems of the wool industry is that as a commodity fibre wool is attracting a steadily decreasing price in global markets. One counter to this trend is to create added-value differentiated products which do not have to be sold as commodities in direct competition with other wools or other fibres.

The generation of niche-market added-value products by chemical treatment in the woolscour is now a major programme in the New Zealand industry. To achieve this is a considerable challenge, as the opportunity to carry out chemical processes in relatively clean liquors is confined to the final bowl of a scour and an immersion time of 30 seconds or thereabouts. Nonetheless a number of differentiated products are already available from scours. These include for example:

FERNplus APB™ - a process for preventing photobleaching of wool products in sunlight behind glass, achieved by adding a specially selected chemical with yellowing characteristics which neutralise the photobleaching of the natural yellow pigments in wool.

FERNplus EP™ - a process which adds a delustring pigment to the surface of wool, which enhances carpet appearance retention and processing performance, and overcomes some of the disadvantages of coarse lustrous New Zealand wool types.

Larvanil™ - a new generation insect-resist treatment which is especially effective against beetle larvae, and overcomes environmental problems, and species immunity problems, associated with previous pyrethroid-based agents.

Several more in-scour chemical processes are under development, as well as others which involve fibre blending and other physical processes. FERNplus□ is a New Zealand Wool Group trademark for enhanced scoured wool products, related to the Fernmark brand used for consumer promotion.

WOOL CARPET YARN WET PROCESSING - THE CHEMISTRY OF SETTING PROCESSES

Machine-made carpets represent the single biggest end-use for New Zealand wool and thus the technology of wool carpet yarns and carpets is of crucial importance to the New Zealand wool industry. Also of considerable importance is the hand-knotted carpet industry of the Near and Far East, and of the Indian subcontinent (including Nepal), which is a major consumer of New Zealand wool.

The manufacture of high quality yarns for the carpet tufting industry provides a significant export outlet for New Zealand scoured wool and considerable scope for further on-shore processing of our raw materials. The yarns are based on 100% wool or 80/20 wool/nylon blends. The yarn manufacturing industry is investing significantly in R&D in New Zealand and is creating technology which establishes a clear competitive advantage for New Zealand spinners. Naturally much of this recent research, carried out at WRONZ, is not in the public domain. Suffice to say, it covers a number of areas of fascinating and novel chemistry, coupled with more efficient processing techniques. Some of the basic aspects of what is openly published are covered below.

A special feature of the New Zealand carpet yarn industry is its concentration upon 'spinning in oil' (ie, using a spinning lubricant, usually a polymer or copolymer of ethylene oxide, to maximise the efficiency of fibre conversion to yarn), followed by wet processing operations which clean and set the yarn. Such wet processing techniques are highly advanced in New Zealand, and are the focus of much of the chemical R&D effort.

Increasing consumer product standards demand manufacturing methods which ensure absolute uniformity of quality within and between successive yarn batches. This is particularly true of yarns intended for plain pastel-shade carpet or for carpet which is to be 'piece-dyed', ie, dyed as tufted carpet fabric usually in a continuous dyeing or printing machine. Such dyeing methods incorporate vigorous washing-off processes and so require well set yarn, i.e. yarn in which the torsional forces due to twisting are thoroughly relaxed so that when the yarn is cut the structure of the yarn remains stable and the tufts of the carpet do not untwist.

In addition, the yarn must be thoroughly cleaned during manufacture, to remove residual dirt and woolgrease, detergent residues, and the processing lubricant added to the loose wool to enable it to be efficiently spun. Other chemical processes, such as insect-proofing, may also have to be included. These wet-processing operations may be efficiently combined into a single operation either in a tape scouring machine which processes hanks or in the modern derivative, a package-to-package continuous yarn processing machine (previously referred to as a 'Chemset™' machined and now marketed as Twistset™).

Some Aspects of Yarn Scouring

Yarn scouring removes from the yarn the processing lubricant, along with traces of residual woolgrease, dirt and dust from the yarn making operations, and residual dirt not fully removed in the original raw wool scouring operation. To scour yarn, either nonionic or, less commonly, anionic detergents may be used. The most common type is of the nonylphenol ethoxylate (NPEO) type, as shown in **Figure 12**. For many years types with about 9 moles of ethylene oxide condensed in the hydrophilic moiety ($n = 9$ in formula) were used, as in raw wool scouring. However, in research at WRONZ it became clear that such detergent solutions had some very undesirable properties - the wool yarn, once having been wet out in such a solution and squeezed, could not be easily wet out again, because of a strong tendency to entrain air. **Figures 13** and **14** illustrate the type of behaviour found on repeated immersions of yarn bundles in solutions of detergents of various concentrations and ethylene oxide chain length. The solution to this problem, from **Figure 14**, is simply to select a detergent with a longer hydrophilic chain. Following this work, NPEO 15 detergents became the industry standard.

More recently alcohol ethoxylates have been introduced into use, because of their easier biodegradability in effluents. One major company in New Zealand, which markets its carpets under an Environmental Choice scheme, has converted all its wool and yarn scouring operations to alcohol ethoxylates for this reason.

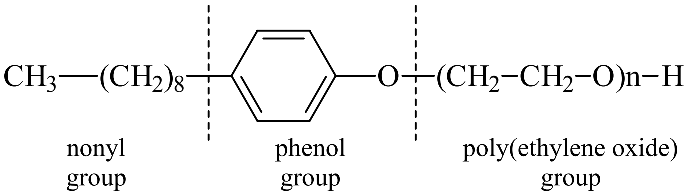


Figure 12 - Nonylphenol poly(ethylene oxide)

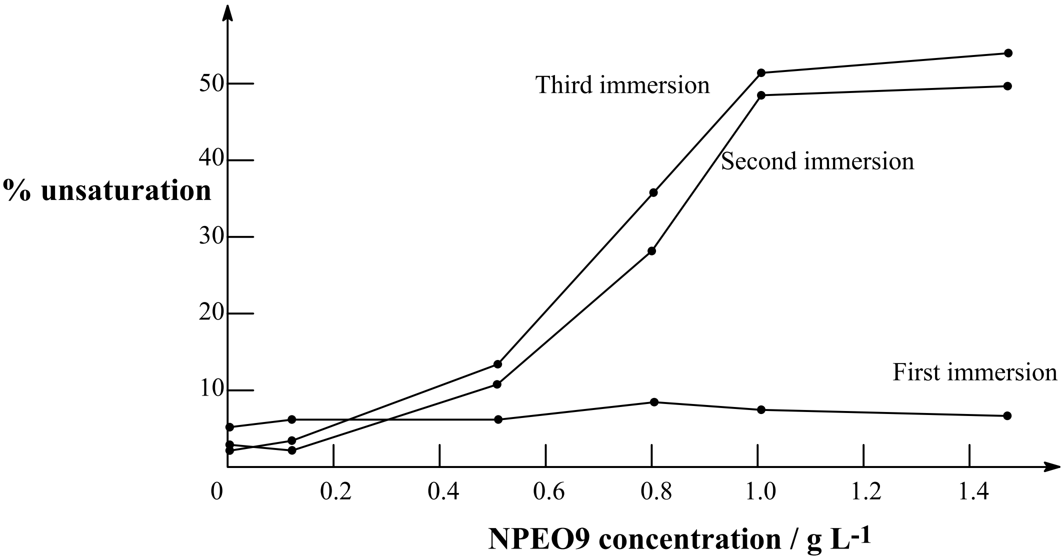


Figure 13 - The degree of unsaturation, defined here as the total free volume of the yarn bundle occupied by air after immersion, as a function of NPEO9 concentration at 50°C for repeated immersion

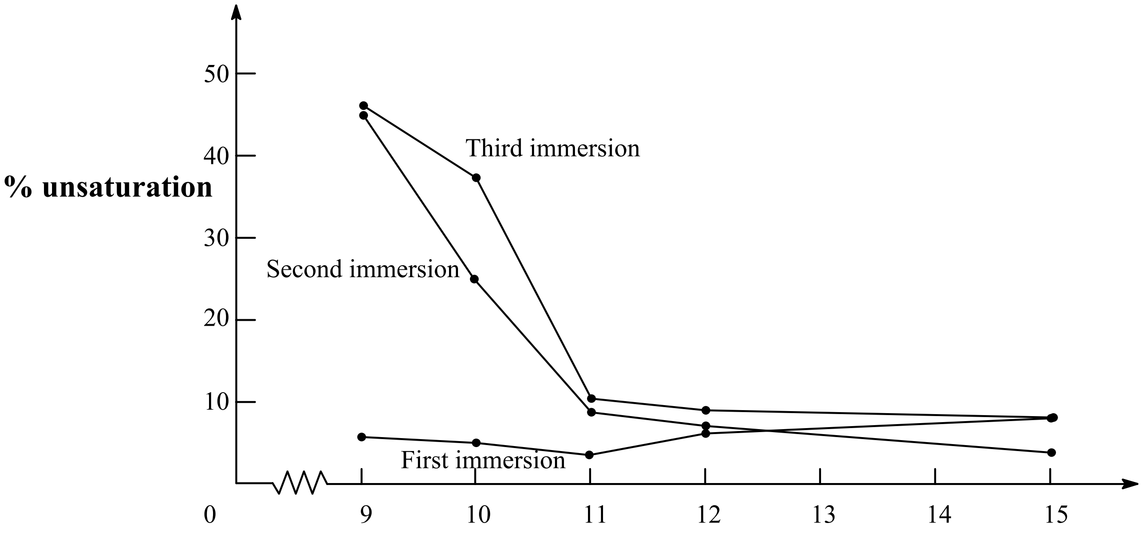


Figure 14 - Dependence of percentage unsaturation on ethylene oxide number of alkylphenol ethoxylates (1 g L^{-1} detergent at 50 °C)

Setting of Wool

Wool is composed of a complex assembly of proteins of different types. At the supramolecular level of organisation the structure consists of highly organised fibrillar aggregates of proteins (the microfibrils) set in a matrix of globular-type proteins of much less discernible order.

In the microfibrillar regions individual protein chains exist as α-helices stabilised in part by intrachain hydrogen bonds. The α-helices in turn are aggregated into 2- and 4-chain units within the microfibril. At the molecular level the fibre is stabilised by inter-chain cross-links formed by the disulphide bridges of cystine residues and by inter-chain secondary bonds, such as hydrogen bonds and salt linkages (especially between —COO^- and —NH_3^+ groups).

Cross-linking of the protein through disulphide bonds is a key feature of wool structure and chemistry. However, most of the cystine is in the matrix proteins and the majority is almost certainly locked up in intramolecular disulphide bonds. It is only a minority of the cystine, in special regions of the wool proteins, that is involved in the physical effects of the disulphide bond chemistry discussed below.

Setting is a process through which a deformed polymeric material is stabilised in its deformed shape by chemical bond interchange. Generically, such a process is referred to as chemical stress relaxation; it commonly involves the relief of stress through the breaking and reformation of molecular crosslinks. Such processes are well characterised in many synthetic elastomers (ie, rubbers). In wool fibres a particularly elegant and simple form of this process occurs through the breaking and reformation of disulphide bonds, in which the scission and crosslinking reactions occur in the one process.

There are four component steps in any setting reaction of a polymeric material. These are listed in **Table 1**, the left hand column giving the general description of the step, the right hand column describing the particular operation that applies to carpet yarns (which are the principal focus of this article). The fourth step in this process tests the stability or permanence of the stabilised configuration, and is an important practical aspect of setting processes.

Table 1 - Four stages of a setting operation

General operation	**For carpet yarns**
1. Deformation	1. Spinning and ply-twisting
2. Stress relaxation ('setting')	2. Decay of torsional forces
3. Release from external stress	3. Cutting of carpet pile
4. Set release (testing permanence of residual defomation)	4. Subsequent processing (piece dyeing) or use (cleaning, wear)

Although disulphide bond reorganisations are in practice the most important setting reactions in wool, it is important to recognise that other forms of crosslinks can also be formed under particular setting conditions. Thus, if deformed wool fibres are treated at high temperature and pH, modifications to the amino acids cystine, glycine, and lysine occur to form modified di-amino acids, lanthionine and lysinoalanine (**Figure 15**). These form stable non-interchanging crosslinks which result in comparatively permanent setting. Disulphide bonds are always amenable, under appropriate conditions, to on-going scission and reformation, so

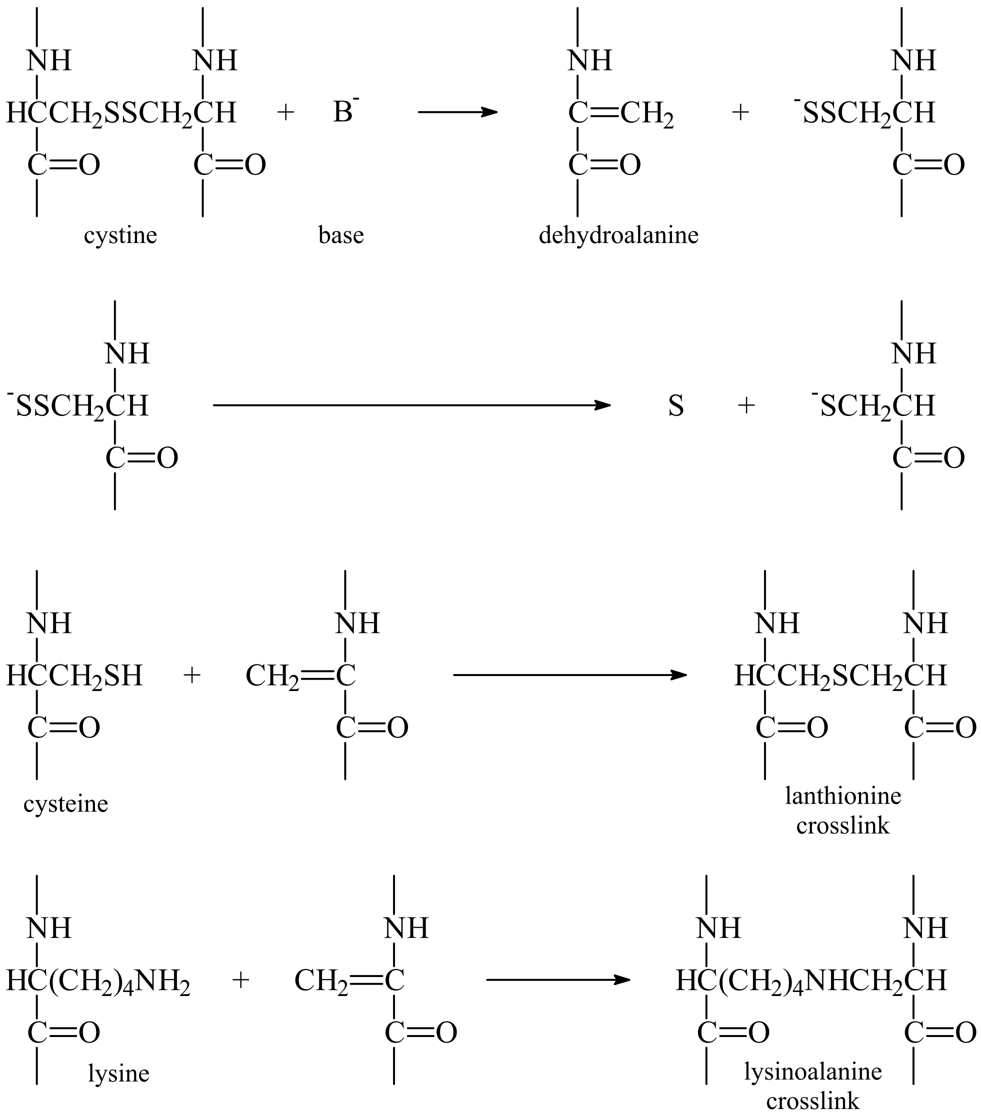


Figure 15 - Stabilizationof strained wool fibres at high temperatures and alkaline conditions by new protein crosslinks

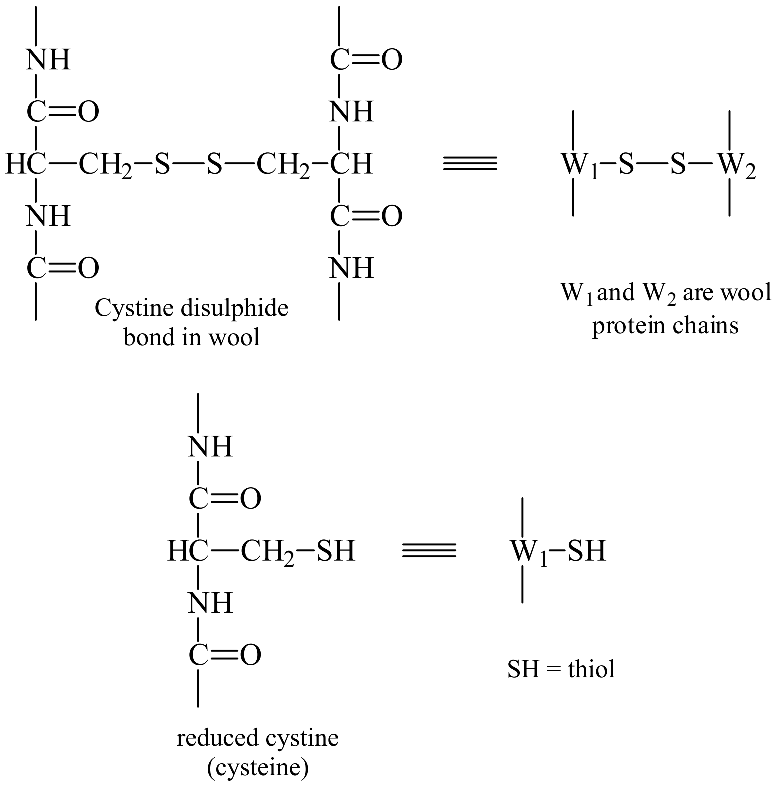
give a set best described as semi-permanent. Finally, the high concentrations of hydrogen bonds (many involving water molecules), polar interactions, and ionic bonds ('salt links', eg, between —COO^- and $^+NH_3$) form yet another cross-linked network of very weak labile bonds, easily rearranged by water or mild heating, which can however, impart to the dry fibre a temporary set (known in wool science as 'cohesive' set).

Although all these levels of setting processes are very relevant to wool technology, we shall discuss below only disulphide bond setting.

Thiol-disulphide Interchange

The process of chemical stress relaxation by thiol-disulphide interchange was initially very well characterised in commercial synthetic polysulphide rubbers (commonly known as 'Thiokols', after the manufacturing company). This explanation was subsequently adapted to explain the practical setting behaviour of wool. The process is schematically set out in **Figure 16**, where two wool protein chains W1 and W2 crosslinked via the disulphide bond of cystine are represented by W_1SSW_2. W3SH is another protein chain in which the cystine is present in its reduced form, the -S-S- group being reduced to -SH. In any disulphide bond network it is assumed there will always be (for equilibrium or steric regions) a small concentration of thiol groups in equilibrium with the disulphide bond. The -SH group is mildly acidic, so at pH > 5, the -SH group is largely ionised to $—S^-$.

It is predominantly the anion from the thiol group which attacks the disulphide bond, forminga new disulphide bridge and another thiol anion. It is a precept of chemical stress relaxation theory (borne out by correct prediction of experimental results) that the new network chain is created on average in a stress-free condition; the process therefore substitutes network chains in a state of mechanical stress with chains which do not bear stress. As the process proceeds, the stress in the material progressively diminishes and eventually results in the stabilisation of the material in its deformed state.



$$W_3SH \rightleftharpoons W_3S^- + H^+$$

$$W_3S^- + W_1S—SW_2 \rightleftharpoons W_3S—SW_2 + W_1S^-$$

Figure 16

However, disulphide bond reorganisation will not relieve all the stresses in a severely deformed wool fibre; other internal stresses may exist, for example from helical segments which have been extended into a sheet configuration. Thus, when a 'set' wool structure is subjected to a set-release process, such as agitation in hot water, these other processes may again impose stresses on the disulphide bond network causing it to relax with the removal of some of the initial set, and a partial return to its original configuration. Thus to stabilise the set, disulphide bond rearrangement after the stress relaxation process must be minimised.

"Chemical" Setting by Cystine Reduction

The factors controlling all practical wool setting reactions are summarised in **Table 2**.

Table 2

Rate-determining parameter	**Controlling factor(s)**
Concentration of thiols/thiolates	Extent of reduction of -S-S- to -SH / $-S^-$
Ionisation of thiol groups	pH
Chemical rate constant activation energy	Temperature
Steric factors, accessibility of reagents, rate of molecular reorganisation	Temperature, water content, (H-bond exchange)

The rate of the stress-relaxation reaction is proportional to the concentration of thiolate [$—S^-$] ions and the concentration of cystine crosslinks [WSSW], the latter being essentially constant. It also depends on the pH, being depressed at acid conditions where the thiolate anion is protonated. It can be accelerated by reactions which reduce disulphide bonds to thiols (i.e., cystine to cysteine). Many reducing agents may be employed for this, but in practice the cheapest and simplest is sodium metabisulphite ($Na_2S_2O_5$ in solid form - MBS for short). In solution this gives 'bisulphite'[1]. The following reactions occur when wool is treated with bisulphite.

$$W_1S—SW_2 \ + \ HSO_3^- \ \leftrightarrows \ W_1S—SO_3^- \ + \ W_2SH \quad \text{(reduction)}$$

(S-sulphocysteine residue)

$$W_2SH \ \leftrightarrows \ W_2S^- \ + \ H^+$$

$$W_3S—SW_4 \ + \ W_2S^- \ \leftrightarrows \ W_2S—SW_3 \ + \ W_4S^-$$

An accelerated setting process using bisulphite (commonly referred to as 'chemical setting') enables setting to be carried out sufficiently quickly, and with sufficiently simple and reliable control procedures, to be adapted to a continuous industrial process. By contrast, other procedures not employing reduction, such as boiling or steam autoclaving, tend to be slow, damaging to the wool, or associated with inherently variable batch operations.

If reducing agents such as bisulphite are left in the wool, although the initial set may be good, any subsequent application of stress or a 'set-release' process will result in the accelerated release of set caused by the same disulphide interchange reaction. To reduce set release to a minimum, reducing agents must be removed, and as many thiol groups as possible reoxidised to disulphides. The latter is particularly desirable in order to restore the mechanical strength of the network. In some setting processes, reducing agents are removed by after-treatments

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[1] In fact, at pH 7, the predominant species in this solution is the sulfonate anion HSO_3^-, hence the quotation marks.

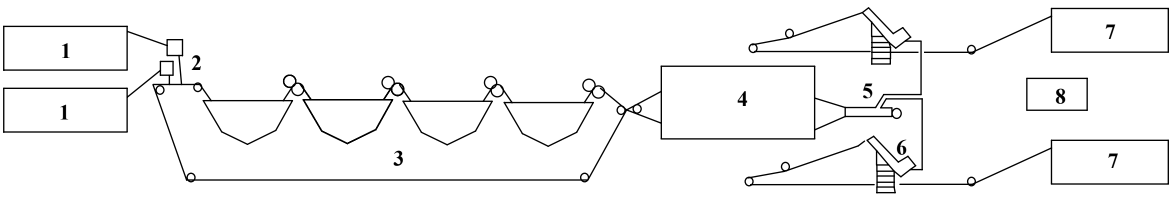
with oxidising agents (eg, perborates) but in the case of carpet yarns it has been established that high-temperature rinsing is sufficiently effective, and this is used in the commercial process described below.

Industrial Application

Beginning in 1971, WRONZ introduced into the New Zealand carpet yarn industry chemical setting processes for setting yarn on a continuous basis during yarn scouring operations. Initially this was carried out in the old tape scouring machines of the day, and the process is still extensively practised in modernised tape scours which process the yarn in the form of hank (skeins). However, in the late 1970s it was realised that there were large economies to be made by converting this process to a 'package-to-package' basis, i.e., running the yarn through the process from a twisting machine bobbin to a tufting machine cone without making hanks as an intermediate product stage. This concept led to the 'Chemset™' machine (since renamed Twistset^{TM}) which has been in commercial operation since 1986. This machine was jointly developed for the global wool carpet yarn industry by WRONZ and Annett and Darling Ltd (now ADM Group Ltd.) of Timaru (ANDAR). **Figure 17** shows a schematic layout of the ANDAR-WRONZ Chemset machine.

Recent versions of this machine continuously process two 'blankets' of coiled yarn each containing 18 yarn ends (18 because textile winders, etc., commonly come in modules of 6). Yarn packages from a twisting machine are loaded onto a creel (top and tailed for continuous running), whence the yarn is processed in two groups of 18 ends through coiling heads which lay continuous blankets of yarn onto a conveyor belt. The yarn is then conveyed through a sequence of four wet processing bowls, each equipped with an efficient squeeze press. The first bowl acts as a yarn scouring bowl, and usually contains a nonylphenol ethoxylate scouring surfactant with an average ethylene oxide chain length of about 15, at about 0.4 - 0.5 g L^{-1}. The second bowl is the 'chemical setting' bowl containing the 'bisulphite' solution, at 5 - 10 g L^{-1} based on anhydrous $Na_2S_2O_5$. The final two bowls are high temperature rinsing bowls, which reverse the equilibrium reaction of bisulphite with wool by washing away the HSO_3^-, thus reforming disulphide bowls. After emerging from the process bowls, the blankets are dried on a high-intensity flatbed dryer, uncoiled, wound into an accumulator (to provide buffer storage during brief plant stoppages), and then taken through a yarn separation zone to automatic winding machines which produce yarn packages for carpet tufting. Machine throughput is typically 300-500 kg hr^{-1}, depending on yarn linear density.

Table 3 lists some of the key operating parameters for such a machine three typical types of yarn production. These operating conditions are modified for different yarn types. Dyes used must be resistant to bisulphite reduction, and also resistant to leaching by the high temperatures and salt concentrations in the process. With 'mixture' yarns (marls, heathers, etc., containing different shades) it is often necessary to drop processing temperatures to about 65°C to avoid dye-bleeding and cross-staining problems.



1. Creel
2. Two 18-end coilers
3. Four wet-process bowls with main conveyor
4. Unidryer
5. Uncoiler conveyor
6. Superba mat accumulators
7. 18-end autodoffing winders
8. Control panel

Figure 17 - Schematic layout of Andar-WRONZ Twistset™ machine

The plant also contains many engineering features, such as heat recovery, effluent ('flowdown') control, and a counter-flow liquor control system which maintains the bowl liquors in a sufficiently consistent condition to allow lengthy process runs (6 - 7 tonnes of yarn).

Process Control

Control of bisulphite bath concentration and pH is crucial to the quality of the yarn, as is (to a lesser extent) detergent concentration in bowl 1.

Based on the wool throughput and flow of process liquor to waste, simple calculations of chemical addition to the plant may be made to enable metering pumps to be set up to supply detergent and bisulphite solution (neutralised to pH 7 with sodium carbonate) to the bowls.

Table 3 - Typical recommended Chemset™ operating conditions*

Yarn type	**MBS conc., bowl 2 / g L^{-1}**	**Bowls 1 - 4, temperatures / ^{o}C**			
Greige for piece-dyeing	10	60	85	85	85
Stock-dyed plain shade:					
- normal twist	10	60	85	85	85
- hard twist	5	60	85	85	85
Mixed colour (Berber, marl, etc.)	5 - 10	60	65	65	65

* MBS = sodium metabisulphite. Residence time per bowl is two minutes.

Fine tuning of the bisulphite bowl concentration may then be carried out by a titrimetric method such as iodine titration (using starch solution as an end-point indicator).

$$HSO_3^- + I_2 + H_2O \rightarrow 2I^- + HSO_4^- + 2H^+$$

Titration with permanganate is often also used as a control procedure, but users should be warned that the reaction between HSO_3^- and MnO_4^- is a 'non-stoichiometric' reaction, with a mixture of products (SO_4^{2-} and dithionate $S_2O_6^{2-}$) depending on concentrations, pH, temperature etc. Nonetheless, if conditions are strictly controlled the permanganate titration can be used as a control procedure. Very roughly, the stoichiometry under the normal titration conditions is:

$$2MnO_4^- + 6HSO_3^- + 2H^+ \rightarrow 2Mn^{2+} + 4SO_4^{2-} + S_2O_6^{2-} + 4H_2O$$

At the present time (1998), WRONZ is trialling an automatic bisulphite monitor and controller, based on flow injection analysis, for the quality control of the bisulphite bowl. This device has been specifically developed at WRONZ as part of an on-going R&D programme on the enhancement of carpet yarn quality. The flow injection analyser is a multi-purpose machine also suitable for controlling other chemical processes.

Commercial success

Since 1986, nine Twistset^{TM} machines have been installed in various countries around the world - 4 in New Zealand, and 1 in each of Denmark, Belgium, England, Japan and USA. Two of the earlier machines still process 24 ends, the rest 36. If we work out the production of these machines assuming a high level of utilisation (true in most cases) and an average yarn linear density of 600 tex (ie 600 g km^{-1}), a figure for annual production of some 18 million kg is arrived at. The installed Twistset^{TM} capacity thus has the potential to process some 25% of the New Zealand wool fibre entering the carpet industry. Even allowing for the fact that not all of the wool processeed is New Zealand wool (especially in Europe), this represents a very significant level of penetration into the industry world-wide, given the diverse nature of the industry and the fact that many products are made by routes which do not require either wet processing or setting.

Effluent Management from Wet Processing

Carpet yarn wet processing is a significant contributor to the total pollution load from an integrated yarn plant (which usually includes a dyehouse as well). The pollution problem arises largely because of the resistance of some of the processing lubricants and detergents to biological oxidation. The chemical oxygen demand (COD) of such substances as ethylene oxide/propylene oxide block copolymer spinning lubricants, and nonylphenol surfactants is substantial. These compounds render the effluent relatively biologically 'hard', and pose something of a problem in some cases for treatment of mill effluent. Table 4 lists some key parameters of a typical flowdown effluent from a continuous yarn wet processing plant.

Table 4 - Typical effluent parameters for a package-to-package yarn wet processing plant

	Conc. / µg g^{-1}
Flowdown (3300 L hr^{-1})	
BOD, average over several months sampling	750
Total solids	3900
Suspended solids	400
Bowl dumping (3500 L)	
Bowl 2 solids content (maximum levels over a 24 hr sampling period)	
- total solids (mostly MBS)	14 500
- suspended solids	1100

There is a progressive move away from nonylphenol surfactants (which are now banned in some countries) to biologically soft alcohol ethoxylates, which while more expensive and less efficient do not produce the environmental problems associated with alkylphenoxy residues.

Another potentially promising effluent reduction technique is the recovery (for re-use, or burning) of spinning lubricants from the effluent. WRONZ has a research project in this area, which has produced encouraging results, and it is likely that such a process will become a feature of at least some future plants.

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