Basic principles of dyeing wool

Contemporary wool dyeing and finishing
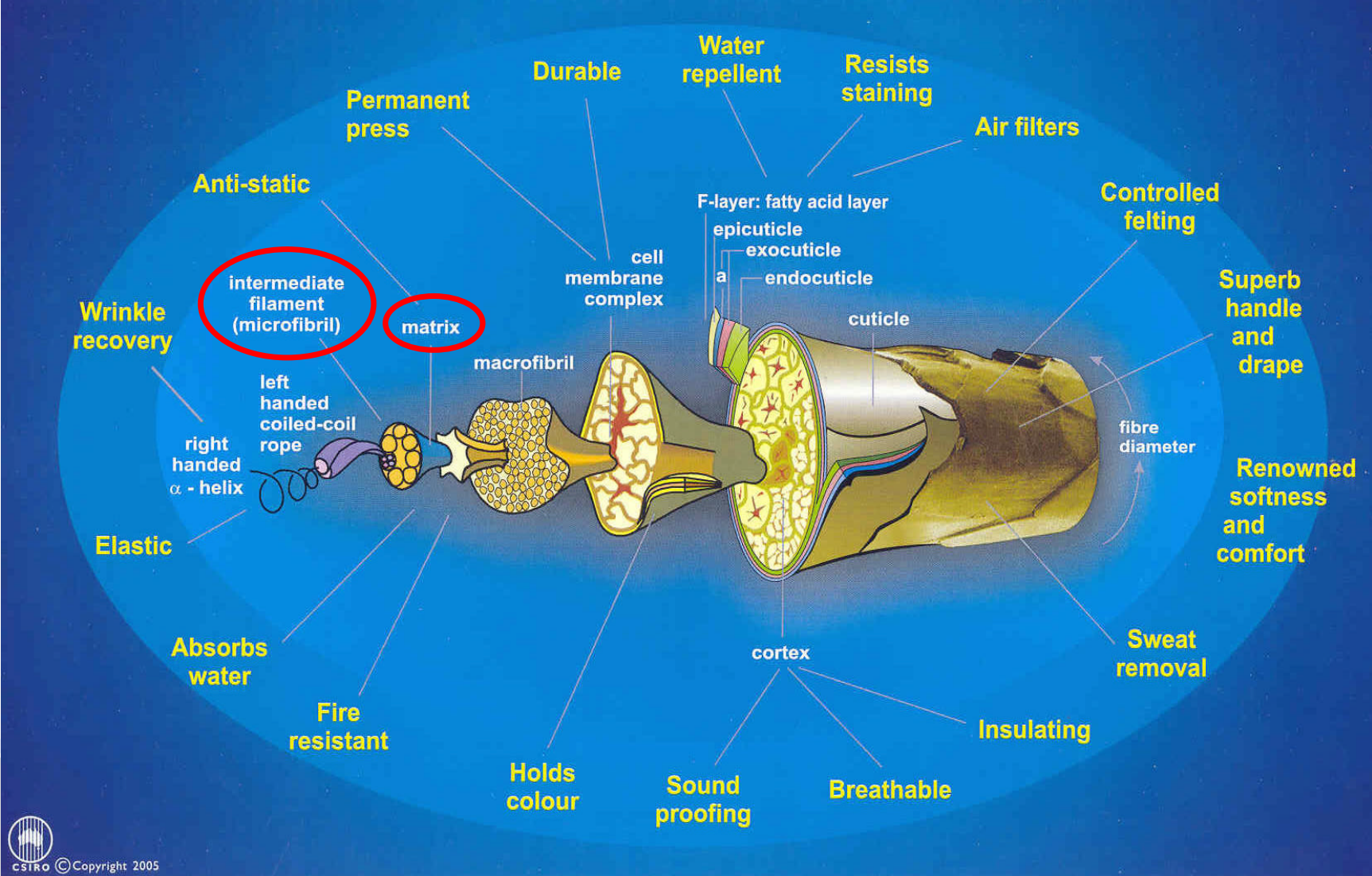
Dr Rex Brady

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Summary

1. Wool fibre structure
2. The mechanisms of dyeing wool
3. Bonding between dyes and wool
4. Thermodynamics of dyeing
5. Diffusion pathways in wool fibres
6. Damage during dyeing

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AUSTRALIAN WOOL
TEXTILE TRAINING CENTRE

1. Wool fibre structure
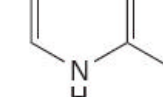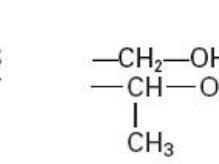
Merino fibre structure
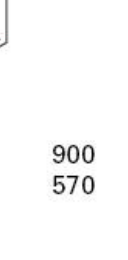
The structure of wool keratin

- Wool is composed of the protein keratin, which occurs in an amorphous form as the matrix and in a crystalline form as the microfibrils.

- Proteins are high molecular weight polyamide polymers composed of different alpha-amino acids, bonded to each other through amide linkages.

- 20 amino acids are found in wool, each with its characteristic short side chain (the functional R group).
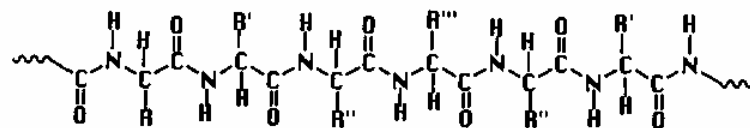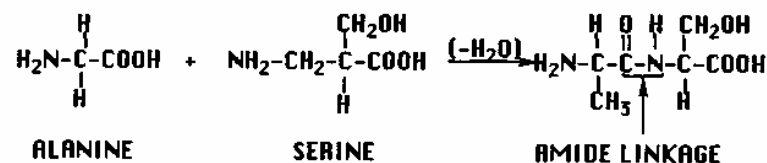
(R, R', R", ... = -H, -CH₃, -CH₂OH, -CH₂-C₆H₅, -CH₂SH, -CH₂-S-S-CH₂-, -CH₂-CH₂-CH₂-CH₂-NH₂, etc.).

Amino acid composition of Merino wool

| Chemical character of side group	Name and abbreviation		Side chain	Concentration (µmol/g)
'Acidic' amino acids and their ω-amides	Aspartic acid	D	$-CH_2-COOH$	200
	Glutamic acid	E	$-(CH_2)_2-COOH$	600
	Asparagine	N	$-CH_2-CONH_2$	360
	Glutamine	Q	$-(CH_2)_2-CONH_2$	450
'Basic' amino acids and tryptophan	Arginine	R	$-(CH_2)_3-NHC-NH_2$ (with $\|$ NH)	600
	Lysine	K	$-(CH_2)_4-NH_2$	250
	Histidine	H	$-CH_2-$ (imidazole ring)	80
	Tryptophan	W	$-CH_2-$ (indole ring)	40
Amino acids with hydroxyl groups in the side chain	Serine	S	$-CH_2-OH$	900
	Threonine	T	$-CH-OH$ ($\|$ CH_3)	570
	Tyrosine	Y	$-CH_2-$ (phenol ring) $-OH$	350

Amino acid composition of Merino wool (cont.)

| Chemical character of side group	Name and abbreviation		Side chain	Concentration (μmol/g)
Sulphur-containing amino acids	Cysteine	C	$—CH_2—SH$	10
	Thiocysteine		$—CH_2—S—SH$	5
	Cysteic acid		$—CH_2—SO_3H$	10
	Cystine		$—CH_2—S—S—CH_2—$	460
	Lanthionine		$—CH_2—S—CH_2—$	5
	Methionine	M	$—(CH_2)_2—S—CH_3$	50
Amino acids without reactive groups in the side chain	Glycine	G	$—H$	760
	Alanine	A	$—CH_3$	470
	Valine	V	$—CH(CH_3)_2$	490
	Proline	P		520
	Leucine	L	$—CH_2—CH(CH_3)_2$	680
	Isoleucine	I		270
	Phenylalanine	F		260

Lindley H, in *Chemistry of Natural Fibres*, ed. Asquith R S, Plenum Press, London, 1977, p 147.

Hydrogen and ionic bonds in wool

- The exact sequence of the amino acids within any polyamide chain is referred to as the **'primary structure'** of the protein.

- The three dimensional arrangement of a polyamide chain is referred to as the **'secondary structure'**.

- The long polyamide chains in the crystalline regions of wool are coiled in a spiral which has the **'alpha helix'** configuration. **This shape is stabilised by hydrogen bonds** formed between the NH and CO groups in successive turns of the helical spiral, as shown opposite.

- The presence of **ionic cross-links** (inner salt formation) also significantly contributes to the stabilisation of the three dimensional structure of wool. These bonds are formed when a carboxylic group and an amino group from two different side chains, along the same polyamide chain or from two adjacent polyamide chains, are sufficiently close to each other.
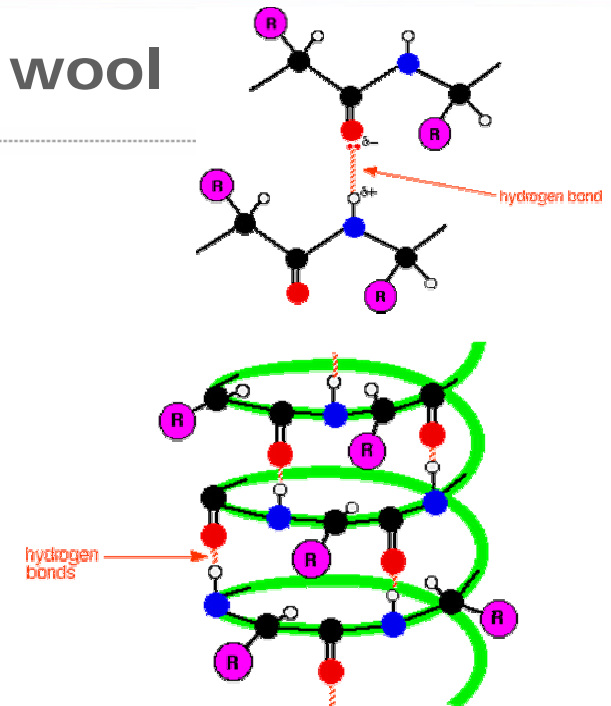

Hydrogen bonds stabilise the alpha helix

Ionic cross-link in wool
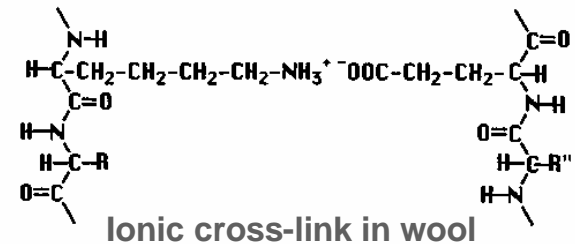
Covalent disulphide bonds in wool

- Wool contains a considerable amount of the amino **acid cystine which provides disulfide (-S-S-)** cross-links within the polyamide chains, as well as between neighboring polyamide chains.
- **Shape retention and strength** of wool depends to a large extent on these cystine linkages.
- When wool is heated in water, particularly at high temperatures, damage is caused by:
  - hydrolysis of cystine cross-links
  - hydrolysis of amide bonds
  - lanthionine formation.
- During dyeing of wool, cystine linkages rearrange and the fibres become permanently set in the shape in which they were dyed.
- When dyeing wool fabrics in the rope form at the boil, they should be continually opened to avoid formation of permanent creases.
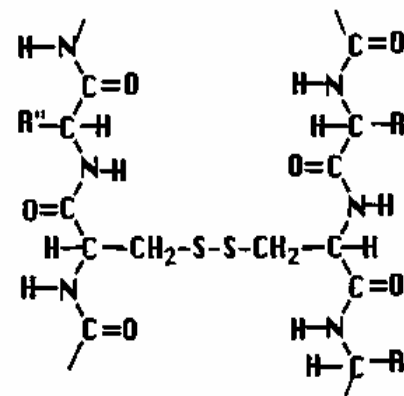
What is textile dyeing?

Dyeing is the decoration of materials using highly coloured substances to enhance their aesthetic appeal.

Why dye textiles?

Recent research in textile marketing has shown that colour contributes about 80% to consumers' buying decisions.

2. The mechanisms of dyeing wool

Wool dyeing can be understood in terms of conventional polymer theory

- Textile fibres are composed of long polymer molecules. Many of the polymer molecules are more or less parallel to the fibre axis.
- A proportion of these molecules are in the form of crystals, while the rest of the polymer is much less structured.
- Fibres can be considered to be made up of tiny, elongated crystals embedded in a less structured web-like matrix of polymer chains.
- In wool, the crystalline domains are the helical microfibrils and the unstructured keratin surrounding the microfibrils is the matrix.

Chrystalline regions
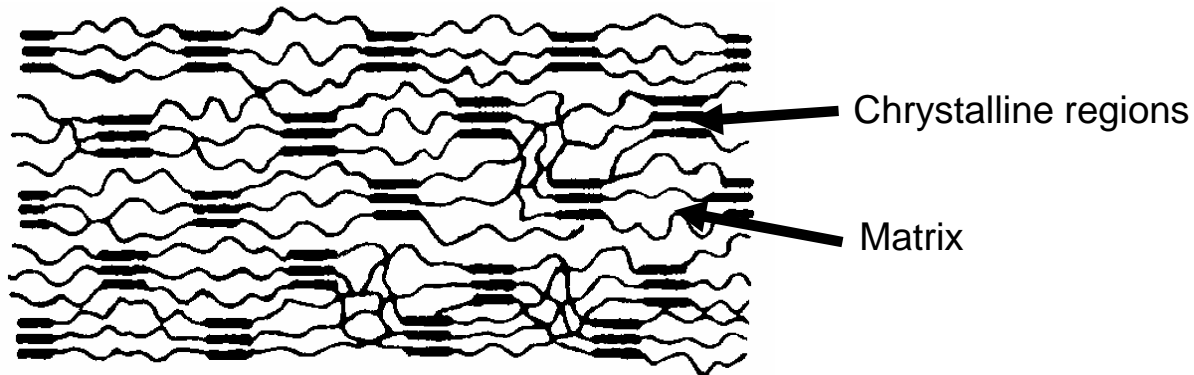
Matrix

Wool dyeing can be understood in terms of conventional polymer theory

- Dye molecules can penetrate the matrix because of its open structure but they can not penetrate the crystalline regions.
- Penetration of dyes is much more rapid when the fibre is above its glass transition temperature.
- Wool is above its glass transition temperature in water at room temperature.
- Potentially wool can be dyed at room temperature but the thermal energy available for diffusion is an issue.

Chrystalline regions

Matrix
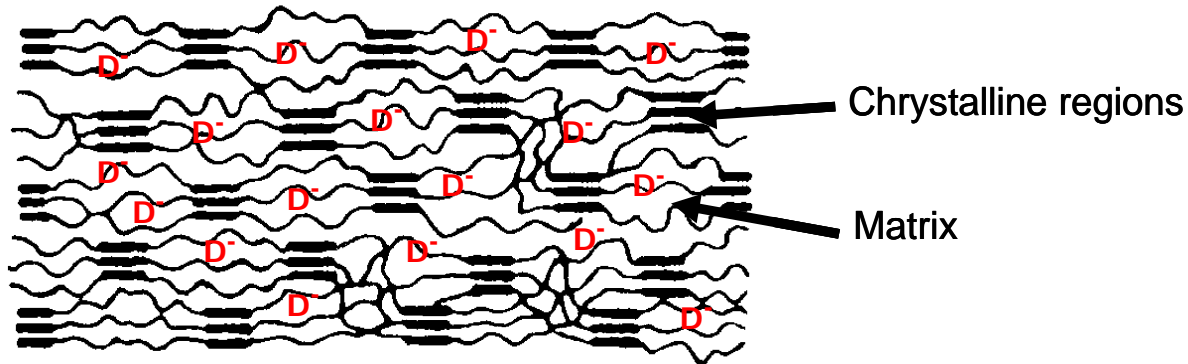
3. Bonding between dyes and wool

Dye absorption sites in wool

Absorption sites in wool are locations where bonds can be formed between dyes and keratin.

- **Ionic bonds** - between oppositely-charged groups.
- **Hydrogen bonds** - between –OH and O=C< groups.
- **Van der Waals bonds** – between polar groups.
- **Hydrophobic bonds** – between non-polar groups.
- **The larger the number of** bonds, the **higher** the **substantivity**. Therefore, larger dye molecules which have more bonds will have better wet fastness.
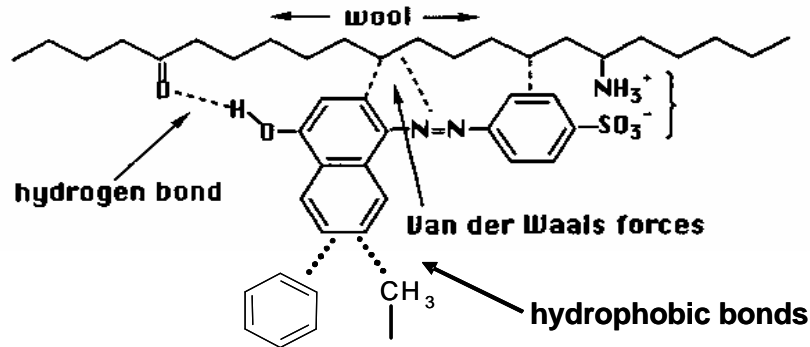
Fixation of reactive dyes

- Reactive dyes can form permanent covalent bonds with free –SH, NH_2 and –OH groups keratin.
- Reaction with amino groups is most likely because their concentration in wool is relatively high.
- Ideally with reactive dyes, covalent bond formation should not occur until even penetration of the dye has occurred.
- However in practice, diffusion, migration and fixation occur simultaneously to various degrees.
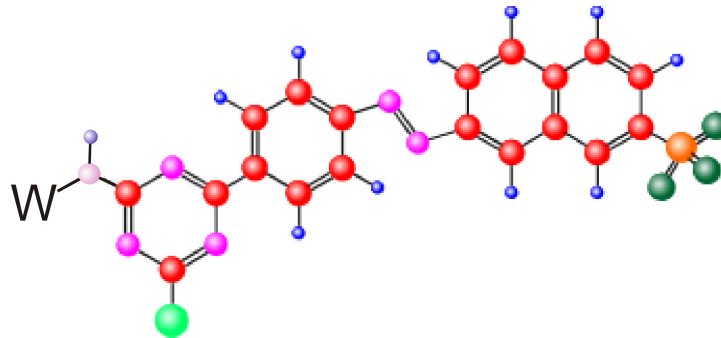
The process of dyeing

Dyeing can be conveniently broken down into a series of stages, depending on the dye:

1. **Movement** of dye molecules in the dyebath to the surface of the fibre.
2. **Adsorption** of dye at the surface of the fibre.
3. **Diffusion** of dye from the fibre surface to its interior.
4. **Migration** of dye between the fibres to achieve an even distribution. This may occur during both the adsorption and diffusion stages.
5. **Fixation** of the dye by covalent bond formation between reactive dyes and the fibre. This may occur during the diffusion stage but is best delayed until as late as possible in the dyeing process.
6. **Aftertreatment** to complete fixation and to remove unfixed dye.

Movement of dye in the dyebath

- Good circulation of dye liquor is essential to produce level dyeings.
- Even circulation is dependant on the mechanical design of the dyeing machine.
- The best type of circulation is high volume, low pressure.
- Modern soft-flow machines give complete dyebath liquor to fibre exchange in 1 to 3 minutes.
- The ratio of liquor volume to the weight of goods (liquor ratio) should be as low as practicable, ie. as little water as possible should be used.

D^- D^- D^- D^-

D^-

D^- D^- D^-
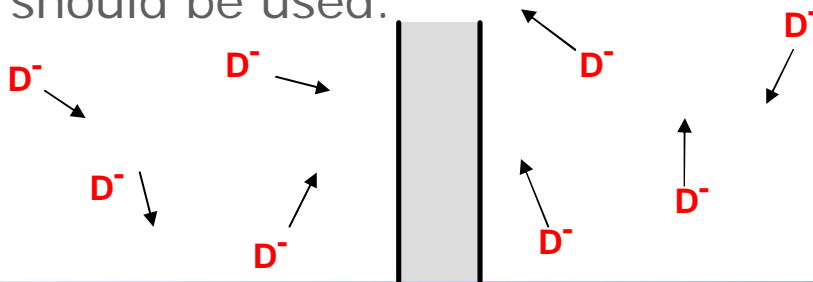
Adsorption

- Once a dye is adsorbed onto the fibre surface, it can begin to penetrate inside the fibre.
- Adsorption can be increased by an opposite charge on the fibre to the charge on the dye.
- Certain dyeing assistants can increase adsorption, presumably by formation of mixed dye-surfactant micelles on the fibre surface.
- Since many dyes molecules are aggregated in solution, (with some dyes up to 300 molecules may be clumped together), these aggregates are presumably adsorbed on the fibre surface.
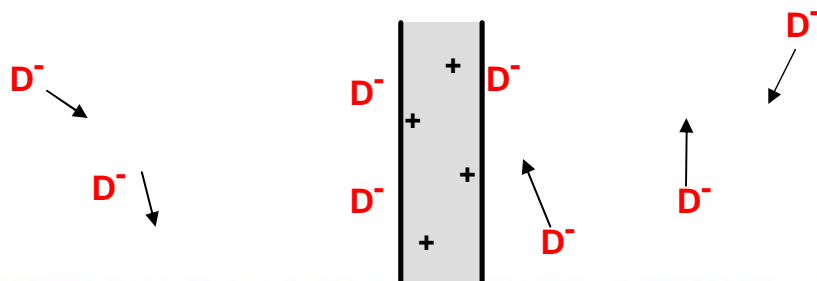
The electrical double layer

- As anionic dyes approach the fibre surface, they must travel through an electrical double layer consisting of more mobile ions weakly adsorbed at the fibre surface.
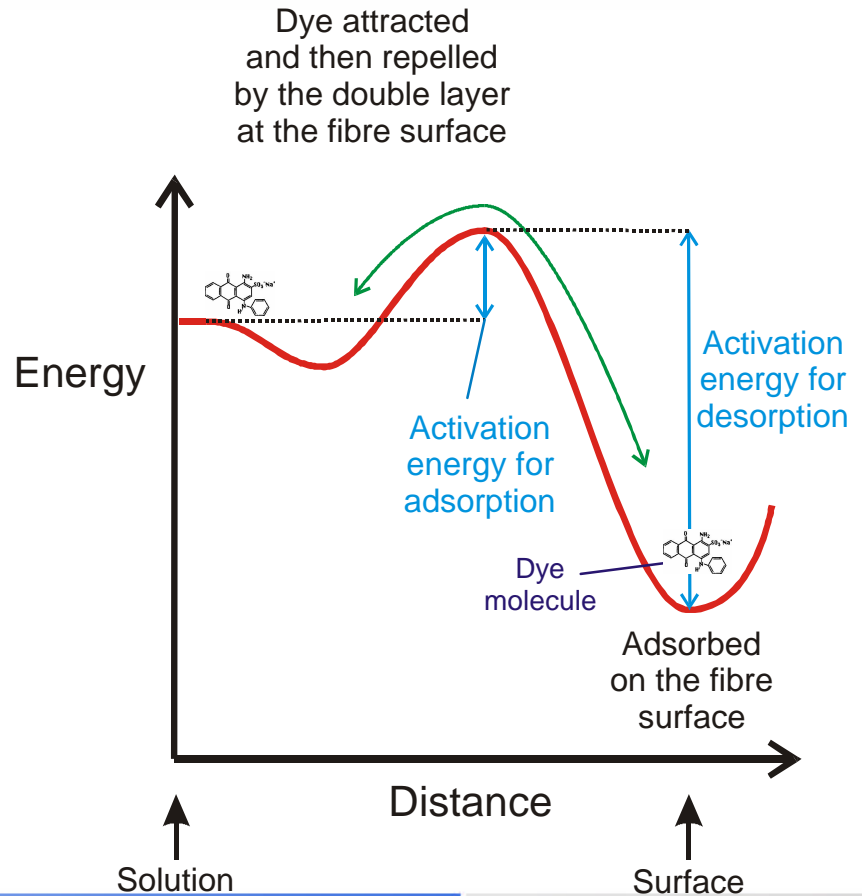- Anions (eg. sulphate, chloride, acetate etc.) attracted to the positively charged fibre (of wool at pH<4) also have associated positively charged cations (eg. sodium) in solution.

Solution   **Fibre**

Electrical double layer
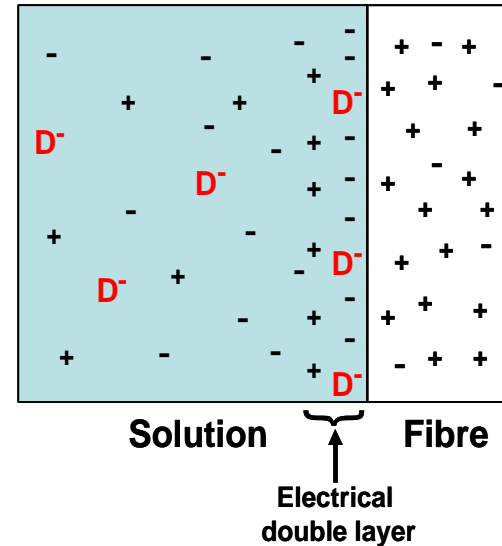
Surface adsorption of dye can lead to rapid exhaustion

- The equilibrium between dye in solution and dye adsorbed on the fibre surface will depend on the relative magnitudes of the activation energies for adsorption (*Ea*) and desorption (*Ed*). If *Ea* << *Ed* , the dye will be strongly adsorbed and exhaustion will be rapid.

- This is presumed to be the mechanism whereby the presence of sodium sulphate in solution reduces the rate of uptake of acid dyes. In this case, *Ea ~ Ed.*

Dye attracted and then repelled by the double layer at the fibre surface

Energy

Activation energy for desorption

Activation energy for adsorption

Dye molecule

Adsorbed on the fibre surface

Distance

Solution

Surface

Diffusion

- Diffusion is one of the fundamental processes by which material moves.
- Dye molecules move within a fibre from areas of high concentration at the surface to areas of low concentration in the interior of the fibre.
- Diffusion is a consequence of the constant thermal motion of atoms and molecules and the energy available depends on the temperature.
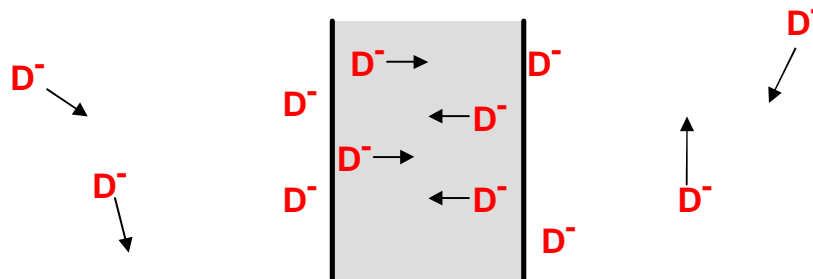
Diffusion

- Aggregated dye molecules adsorbed on the fibre surface presumably must break down into single molecules, because it is unlikely that dyes would be able to diffuse through the keratin matrix except as single molecules or very small aggregates.
- Diffusion occurs by dye molecules 'jumping' from one absorption site to another within the fibre.
- The end result of diffusion is a constant concentration throughout the fibre.
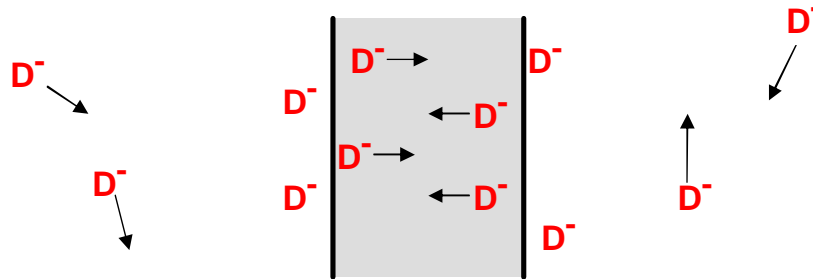
Activation energy for dyeing processes

In an analogy with activation energy, the volley ball must have enough energy to get over the net.
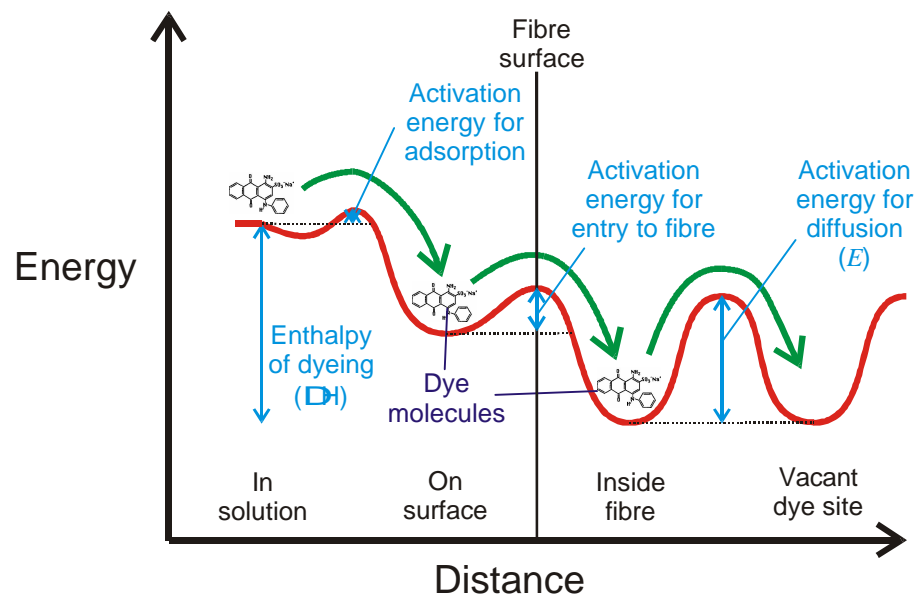
- It is usually assumed that the activation energy for diffusion inside the fibre is greatest, and therefore the diffusion rate determines the rate of dyeing.

- This may not be correct if the disappearance of dye from solution is taken to be the dyeing rate. Dye may be adsorbed strongly on the fibre surface much faster than it diffuses into the fibre.

Diffusion

- When the **dye molecules** penetrate into the inner parts of the fibres they **become associated with dye sites**.

- Dyes with a high substantivity and/or low solubility will tend to be more strongly adsorbed onto dye sites within the fibre and this will result in a slower rate of diffusion.

- Dyeings usually will not achieve maximum durability unless the dye has completely penetrated the fibre.

- Penetration of dye into the fibres can be checked by cutting cross-sections of the fibres with a microtome after embedding them in a suitable resin.

WIRA fibre microtome

Migration

- Heavily dyed fibres, or parts of fibres, lose dye by desorption into the dyebath and dye is taken up from the bath by less heavily dyed fibres, or parts of fibres.
- Dye in the bath comes to equilibrium with dye on the fibres.

$$\text{Dye}_{\text{in bath}} \Leftrightarrow \text{Dye}_{\text{in fibre}}$$

- Migration may be necessary because of unlevel uptake due to poor circulation in the dyebath or to physical and chemical differences between the fibres (eg. tippiness in wool).
- To enhance migration, dyeing is usually carried out at high temperatures. Affinity between dye and fibre decreases with increasing temperature.
- Certain levelling agents are also used to promote migration. Such assistants form complexes with dye molecules in solution, thereby decreasing the rate of dye adsorption lowering the equilibrium exhaustion.
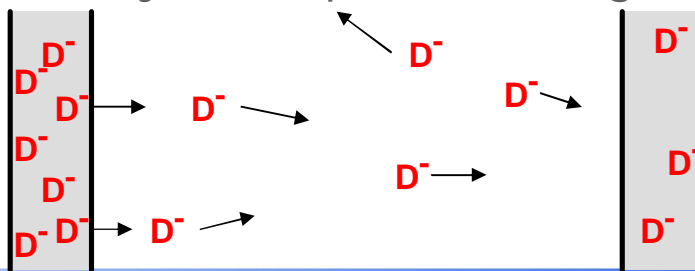
Aftertreatments

Aftertreatments are used to enhance the wash-fastness of the dye by:

- improving the bonding between the dye and the fibre (alkaline aftertreatment of reactive dyes)
- increasing the insolubility of the dye (e.g. with syntans for acid dyes)
- rinsing to remove unfixed dyes and dyeing assistants from the fibres. The procedure may vary from a mild rinse with warm water to the use of a detergent solution with pH control.

Completion of a dyeing process

- After dyeing, if the shade obtained is satisfactory, the dye-bath should be cooled down slowly or dropped while hot.
- Many dyes with low solubility may precipitate upon fast cooling and deposit on the goods. This is not usually a problem with wool if the degree of exhaustion is high.
- With certain fabrics, such as acrylic and wool fabrics, sudden cooling may lead to permanent creases and distortion of their shape.

4. Thermodynamics of dyeing

Dye uptake

- The **degree of exhaustion** refers to the portion of dye taken up by the fibres.
- Exhaustion is a **combination of surface adsorption and diffusion** of dye.
- Very **fast exhaustion** called a 'fast strike', can lead to unlevel dyeing.
- The exhaustion rate of dyes is usually controlled by the rate of rise of temperature of the dyebath and by the presence of dyeing assistants which form complexes with dyes and fibres.
- Most wool dyes have high degrees of exhaustion.
- With wool, high levels of exhaustion may be achieved by lowering the pH towards the end of a dyeing. This increases the positive charge on the wool and the remaining anionic dye in solution is attracted to the fibre.

Dye exhaustion curves
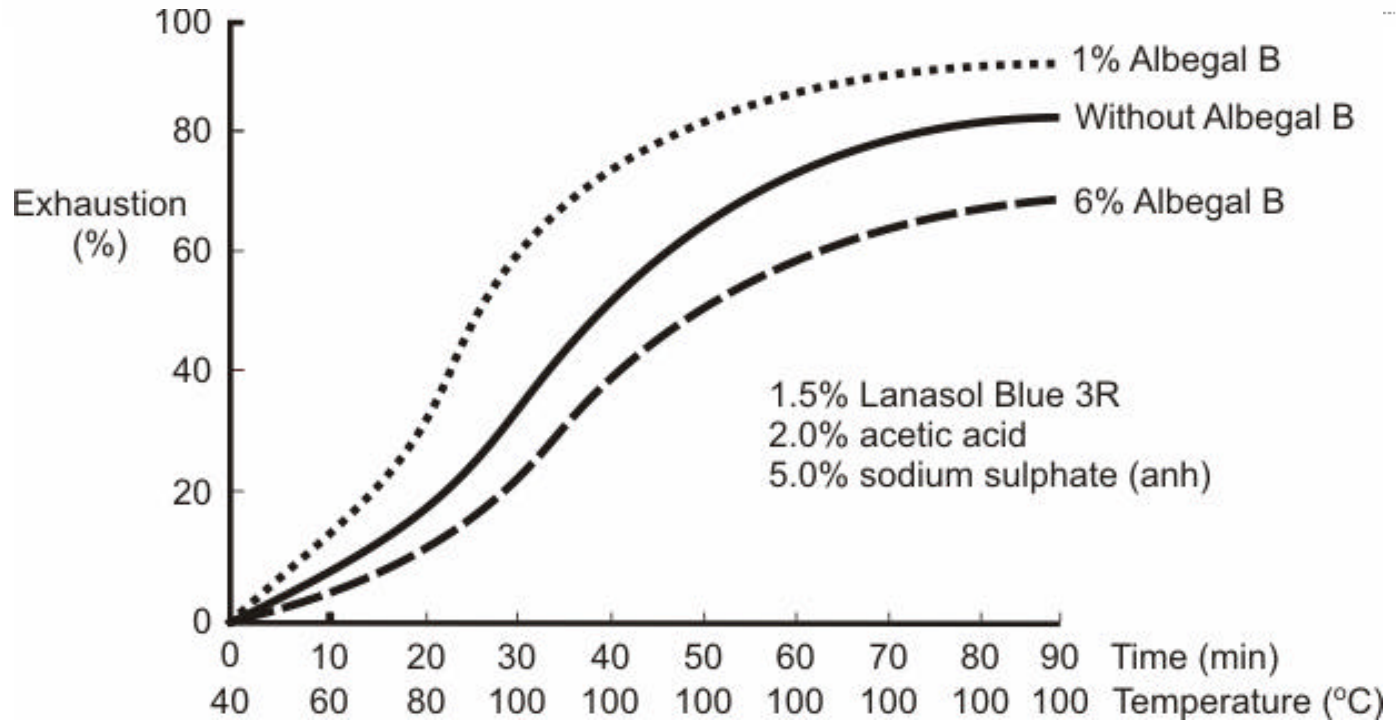
The temperature is raised from 40ºC to 100ºC in 30 min. and held at 100ºC for 60 min. Albegal B increases the uptake at 1% but decreases the uptake at 6% owf.

The affinity of dyes for wool

Affinity is given the symbol $?\mu$ and

$$?\mu = ?H - T?S$$

where $?H$ is the heat of dyeing
T is the absolute temperature
$?S$ is the entropy of dyeing.

- Dyes with high affinity for wool have large negative values of $?\mu$.

- Large negative values of $?H$ are usually obtained with wool, i.e. dyeing is an exothermic reaction.

- $?S$ is also negative since it represents a change from a less ordered system (dye in solution) to a more ordered system (dye absorbed in a fibre), i.e. a net loss of entropy. Hence the term $-T?S$ is positive and reduces the affinity of dye for the fibre.

- The effect of increasing temperature is to decrease the affinity of dyes for wool.

Effect of temperature on exhaust dyeing
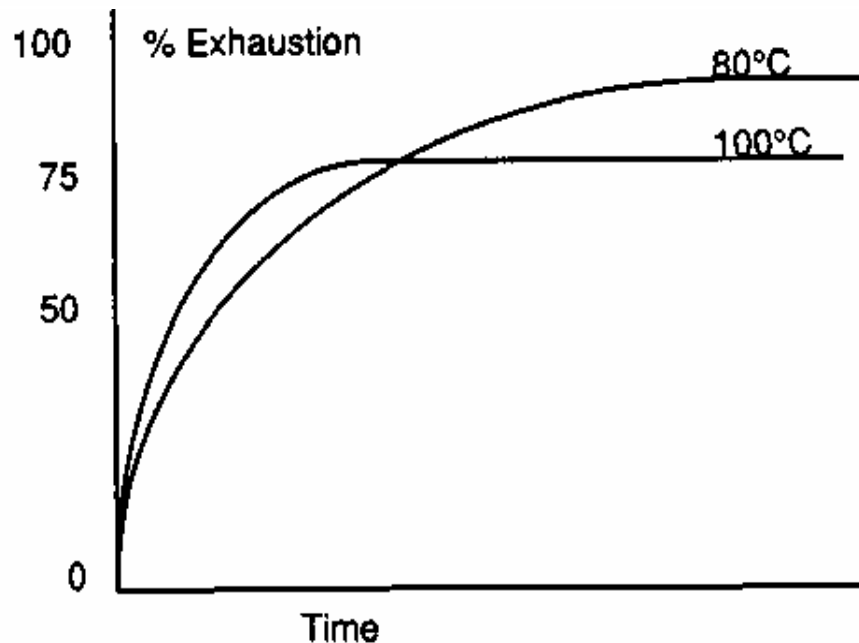
Increasing the temperature of dyeing increases the rate of dyeing, but decreases the percent exhaustion at equilibrium. This is because the affinity of dyes for the fibre decreases with temperature.

Dye absorption isotherms

- These curves show the effect of dye concentration on the distribution of dye between the fibres and the dye-bath, at equilibrium.
- Each isotherm curve corresponds to a single temperature and varying amounts of dye used.

$[D]_f$ = concentration of dye on fibers

$[D]_s$ = concentration of dye in dye-bath
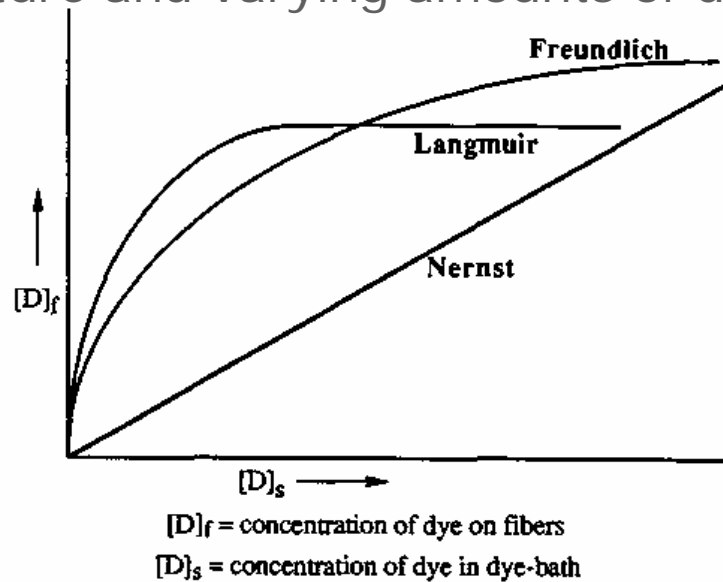
Dye absorption isotherms

- The **Nernst** isotherm represents simple linear partition of the dye between the fibres and the dye-solution. This is found for solution dyeing of some synthetics.

$$[D]f / [D]s = K$$

- The **Langmuir** isotherm shows that the amount of dye absorbed increases as the concentration increases up to the saturation point. This is typical of fibres with a limited number of dye-sites; for example, when dyeing nylon with acid dyes.
- The **Freundlich** isotherm shows that as more dye is added to the dye-bath, more dye goes to the fibres. As the concentration of dye in the dye-bath increases, the amount of dye in the fibres also increases. No section of the curve is linear.
  - The number of binding sites for the dye in the fibre exceeds number of dye molecules under ordinary conditions.
  - As the amount of dye on fibres increases, the sites close to the fibre surface may become blocked and this slows down further penetration of the dye.
- **Wool dyeing follows Freundlich isotherm behaviour**.

Kinetics of dyeing processes

As already indicated, the uptake of dye involves three main processes:

- approach of dye to the fibre
- adsorption of dye on the fibre surface
- diffusion of dye into the interior of the fibre.

All these processes require energy for their initiation, but as we have seen, uptake of dye will occur only if the total system moves from a higher to a lower energy state as a result of the uptake of dye.

Diffusion

- Diffusion is the movement of atoms in a material from high concentrations to lower concentrations.
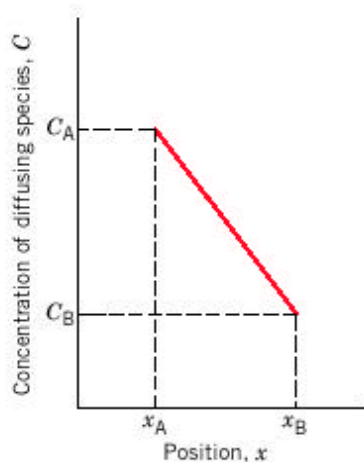
  'Stuff moves from where you have lots to where you have little'.

- Once dye has entered a fibre, diffusion begins the spread of dye throughout the fibre.

- Temperature has a large effect on diffusion, as temperature increases, so does the rate at which the diffusion proceeds.

- The distribution of (non-reactive) dye throughout a fibre will eventually become even if there is sufficient energy and time available.

- Simultaneous covalent reaction of reactive dyes may result in dye becoming immobile before it can penetrate the fibres completely.

Fick's laws of diffusion

Fick's two laws of diffusion are used to study dyeing processes.

Fick's first law of diffusion states that the rate of transfer of dye per unit area of a diffusing material (F) (the diffusive flux) is related to the concentration gradient $\partial c/\partial x$:

$$F = -D\left(\frac{\partial c}{\partial x}\right)$$

Fick's laws of diffusion

Adolf Eugen Fick (1829-1901)
physiologist and inventor

where: c = dye concentration
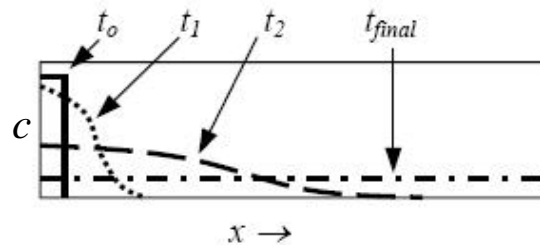x = distance through the substrate
D = constant, the diffusion coefficient.
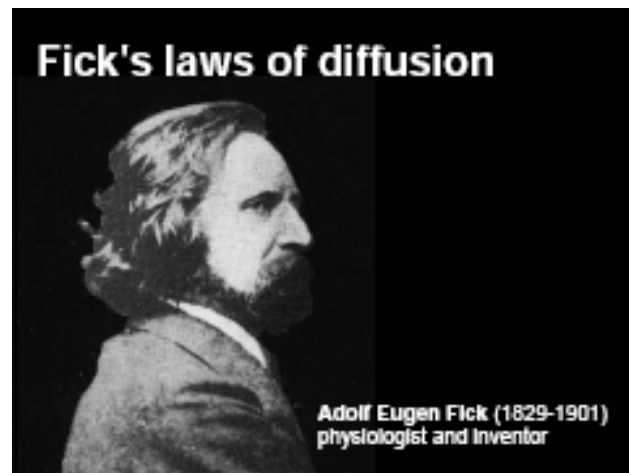
Fick's second law

The variation of dye concentration with time $(\partial c / \partial t)$ more closely represents practical dyeing conditions, and is the basis of **Fick's second law**. In its simplest form this can be written:

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial x^2}\right)$$

In practice, the diffusion coefficient of a dye often varies with concentration (e.g. with direct dyes on cellulose and acid dyes on nylon) and the equation then becomes:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} D\left(\frac{\partial c}{\partial x}\right)$$

How to measure diffusion coefficients

Integration of Fick's second law gives an equation that can be used to determine the diffusion coefficient of a dye at a particular temperature:

$$\frac{c_t}{c_\infty} = 1 - Ae^{-By} - Ce^{-Ey} \ldots$$

where:

c_t = concentration of dye in the fibre at time t

c_∞ = concentration of dye in the fibre at equilibrium

$y = Dt/r^2$

D = diffusion coefficient of the dye

r = radius of the fibre

A, B, C, E, etc. are constants.

Values of c_t and c_∞ can be read off from a rate of dyeing curve. Tables of values of Dt/r^2 for corresponding values of c_t/c_∞ are available, **so values of D can be determined**.

Practical ways of determining approximate diffusion coefficients

The diffusion equation is simplified by choosing the value of t to be the time of half dyeing ($t_{1/2}$).

The time of half dyeing is the time at which the percentage exhaustion is half that at equilibrium ($c_t/c_\infty = 0.5$). Then:
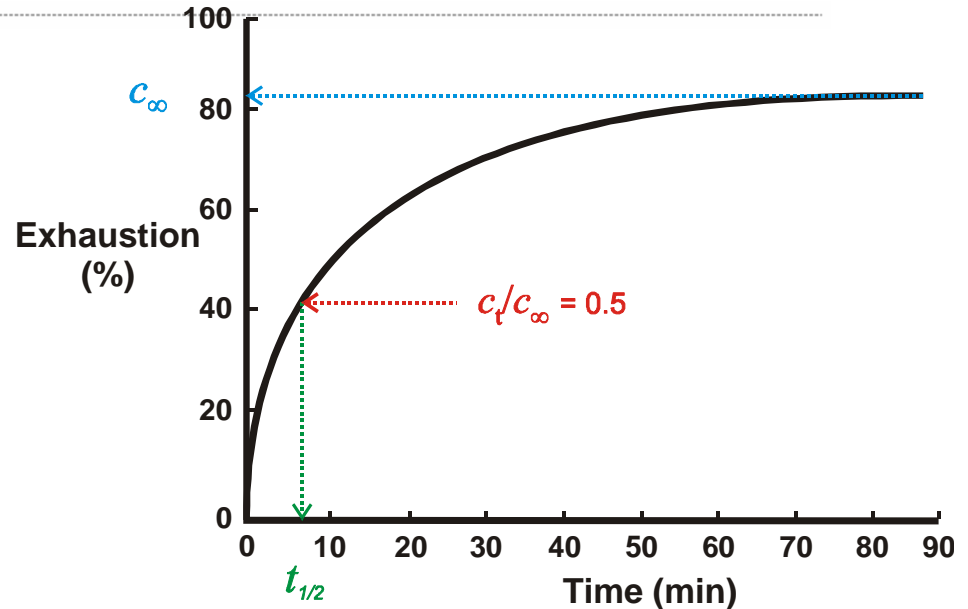
$$D = \frac{0.0492\, r^2}{t_{1/2}}$$

This equation applies to medium-to-long dyeing times.
For short dyeing times:

$$\frac{c_t}{c_\infty} = 2\left(\frac{D\,t}{p}\right)^{1/2}$$

A plot of c_t/c_∞ versus $t^{1/2}$ is linear, with a slope proportional to $D^{1/2}$.

Determining a diffusion coefficient from an isothermal dyeing curve

After the dyeing has come to equilibrium, the time of half dyeing ($t_{1/2}$) can be determined, and knowing the mean radius of the fibres (r), the diffusion coefficient (D) can be calculated.
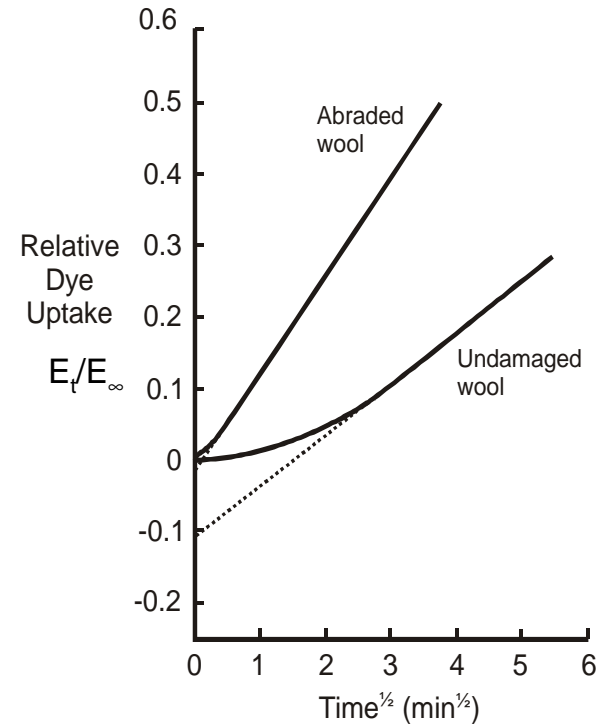
Some diffusion coefficients:

Dye	D (m^{2}s^{-1})	Temperature (°C)	RMM
CI Acid Orange 7	1x10^{-15}	60	327
C I Acid Red 27	5x10^{-17}	35	534
C I Food Yellow 3	6x10^{-15}	50	452

$$D = \frac{0.0492\,r^2}{t_{1/2}}$$

Diffusion studies reveal a barrier to diffusion at the wool fibre surface

- These rate of dyeing curves for short times show different rates of dye uptake for undamaged and damaged fibres.

- The plots are linear, as expected, except for very short dyeing times.

- Extrapolation of the plot for undamaged wool to the ordinate at $E_t/E_\infty = -0.11$ suggests a significant barrier effect at the fibre surface.

- Abrasion of the fibres to remove most of the cuticle cells almost completely eliminated the surface barrier effect.

- The steeper slope of the plot for abraded wool shows that the dye is diffusing faster into the damaged fibres, i.e. the diffusion coefficient is greater.

G. M. Hampton and I. D. Rattee, JSDC, **95** (1979) 396.

Rate of dyeing curve for Azo Rhodamine 2G at 25°C.

The practical significance of diffusion coefficients

- Dyes with high diffusion coefficients have poor wet fastness.
- Dyes with low diffusion coefficients can not penetrate the fibres quickly enough for a practical dyeing process.
- Most wool dyes have relative molecular masses (RMMs) between approximately 400 and 800, otherwise their diffusion coefficients are too low for the dyes to penetrate inside wool fibres in commercial dyeing processes.

Temperature and the rate of dyeing

The effect of temperature on the rate of any process is given by the **Arrhenius equation,** of which this is one form:

$$k = Ae^{-E/RT}$$

where:

k = the rate constant for the process
A = a constant called the frequency factor
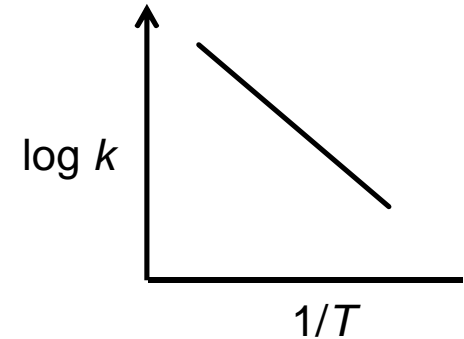E = energy of activation for the process
R = the general gas constant
T = the absolute temperature.

Integrating the above equation gives:

$$\log k = \log A - \frac{E}{2.303RT}$$

Temperature and reaction rates

$$\log k = \log A - \frac{E}{2.303RT}$$

- A plot of log k vs. 1/T gives a straight line with the slope – E/2.303R.
- The rate of dyeing depends on the absolute temperature (T), because **the rates of uptake and diffusion of a dye depend on the heat energy available**.
- It is not possible to heat wool to much higher temperatures than $100^{o}C$ without seriously weakening and yellowing the fibre. So this fixes the highest effective dyeing temperature at $100^{o}C$, unless special protective technology is used. Dyes with high energies of activation for diffusion have low diffusion coefficients.

The effect of temperature (ºK) on dyeing
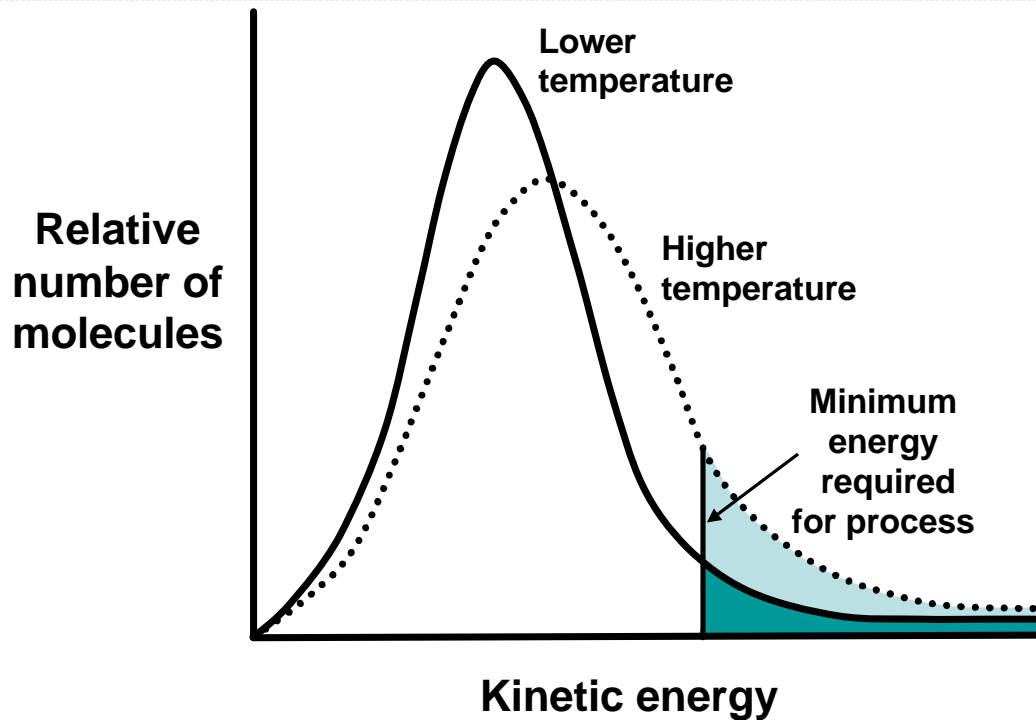
Dyeing rates are greater at higher temperatures because a larger fraction of dye molecules has enough energy to enter and diffuse through the fibres.

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Determination of activation energy for dyeing

We have seen that a plot of log $t_{1/2}$ or log k versus $1/T$ gives a straight line of slope

$$= -E / 2.303 \, R$$

from which an 'activation energy of dyeing' can be calculated. However the interpretation of the value of the 'activation energy of dyeing' may not be straightforward because dyeing can be split into at least three processes:

- approach
- adsorption
- diffusion,

and each of these may contribute to the overall rate at which dye is exhausted from solution.

Parameters that can be controlled during dyeing

- temperature
- circulation of dye liquor
- pH
- addition of dye
- addition of chemicals and dyeing assistants.

Sedomat 5000
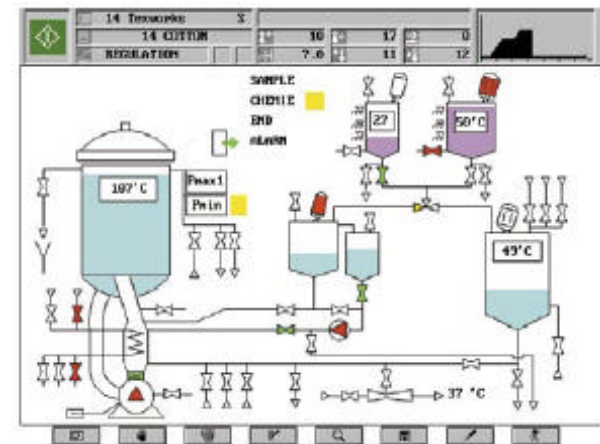
Parameters for optimal dyeing

- **Circulation contact time per minute (min^{-1})**
  - Liquor flow rate (L kg^{-1} min^{-1})/liquor ratio ˜ 1-2 min^{-1}, ie. 1-2 complete dyebath changes per minute
- **Liquor ratio (L kg^{-1})**
  - as low as possible (4:1 to 40:1) to minimise time, energy, water, chemicals
- **Temperature**
  - ± 1°C
- **Temperature gradient**
  - ~ 1-5°C min^{-1}
- **Accuracy of temperature control**
  - ± 1-2°C
- **pH control**
  - ± 0.2 units
- **Rate of dye uptake**
  - ~ 2% per minute
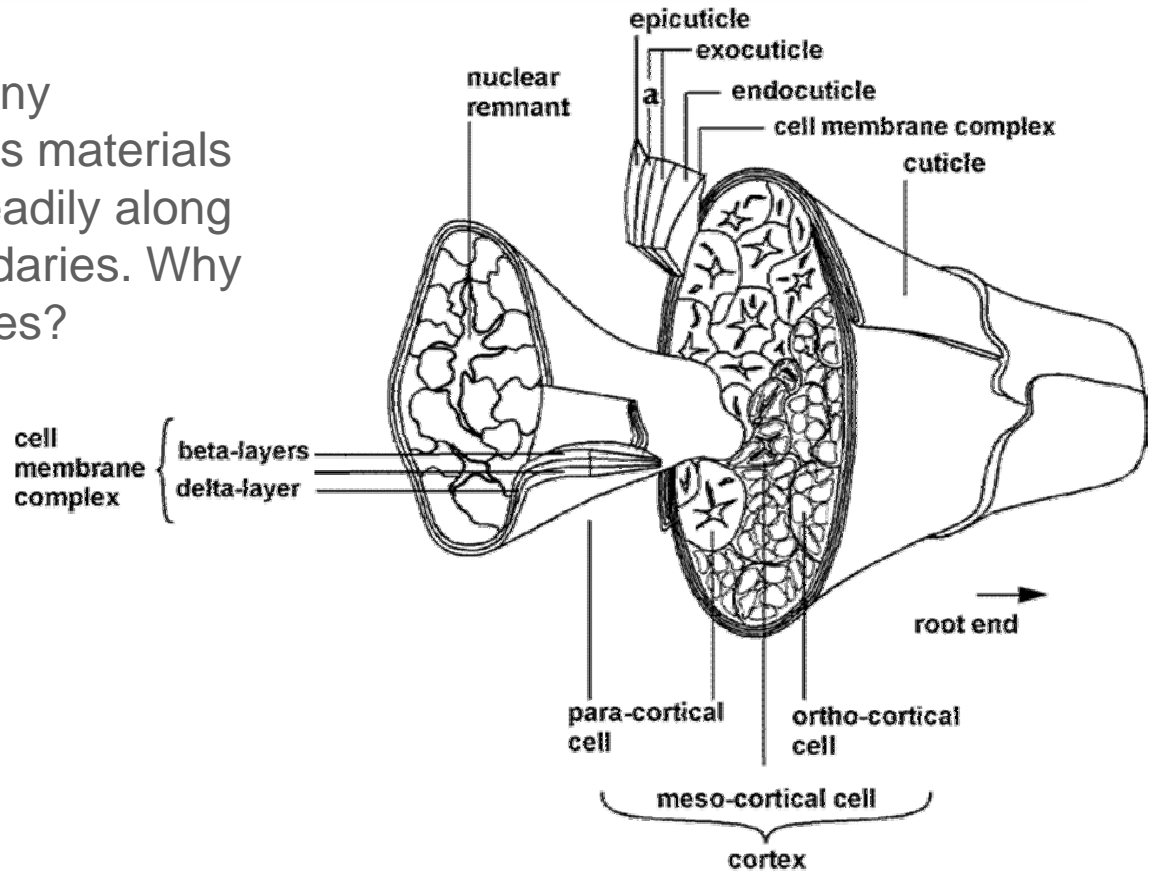
5. Diffusion pathways in wool fibres

How do dyes enter wool fibres?

- Isotropic diffusion
  - Fibre is a uniform, long, thin, cylinder.
  - Assumed in studies up to 1970s based on Fick's law of diffusion.
  - Deviations from ideal behaviour suggested a barrier to diffusion at the fibre surface.
- Anisotropic diffusion
  - Assumes that dye may diffuse differently through various structural components of the fibre.
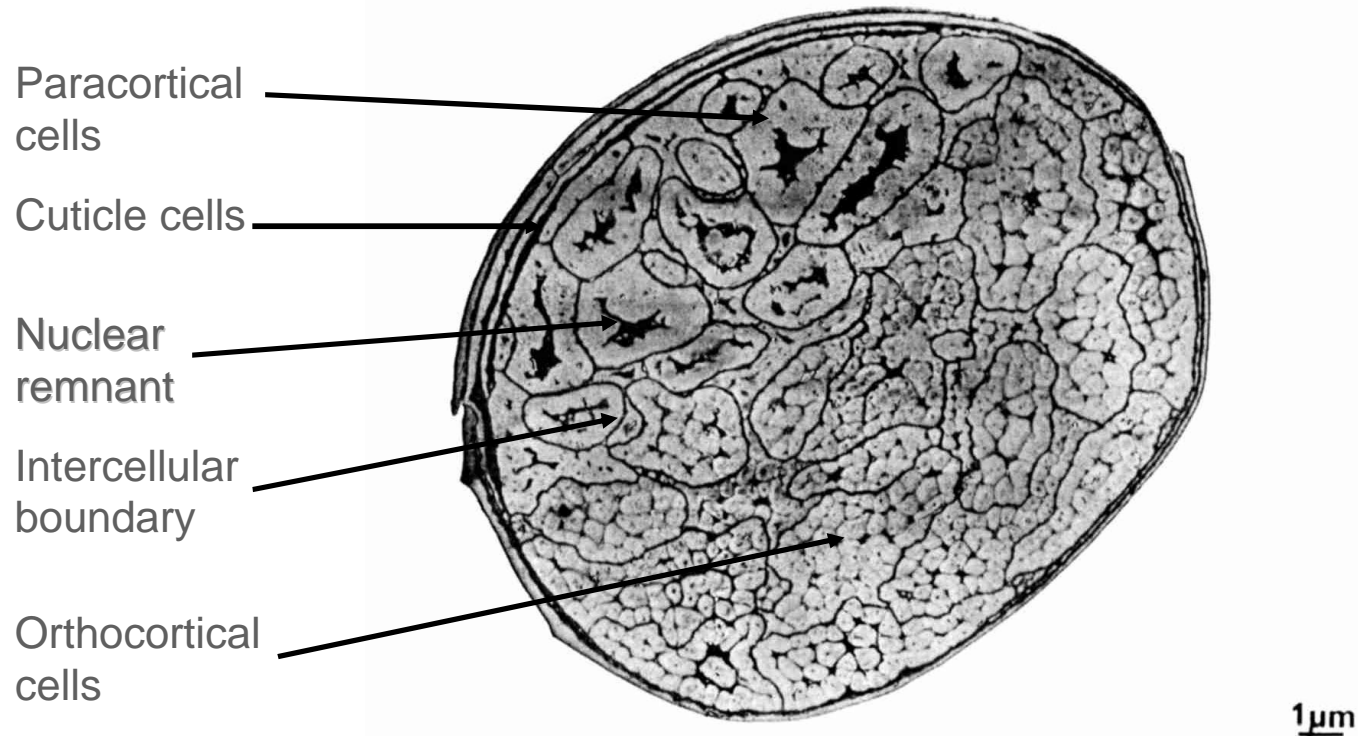   - e.g. faster between the cells than through the cells.
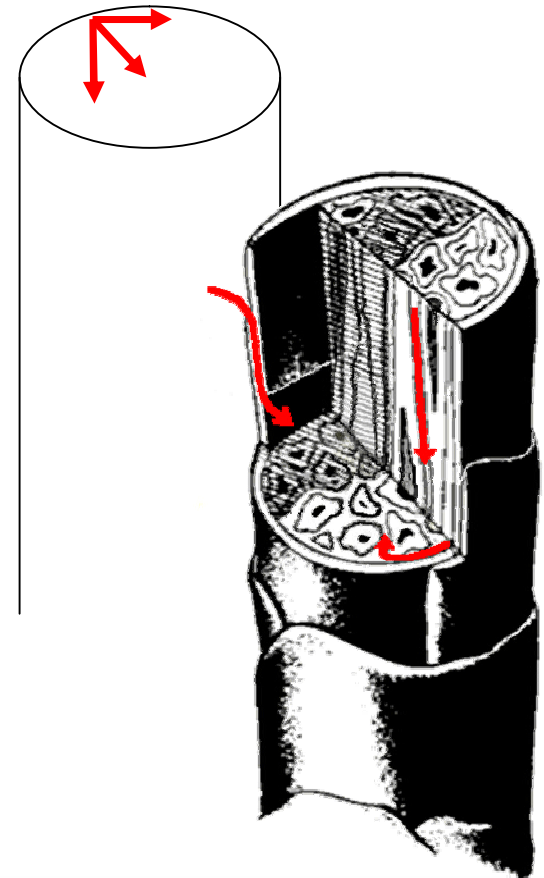
Wool fibre structure

Diffusion in many inhomogeneous materials occurs more readily along the grain boundaries. Why not in wool fibres?

Electron micrograph of a wool fibre

Paracortical cells

Cuticle cells

Nuclear remnant

Intercellular boundary

Orthocortical cells

1µm

Reference: D F G Orwin, J L Woods and S L Ranford, Aust. J. Biol. Sci., **37** (1984) 237.

Seeing dyes

It is very difficult to see ordinary dyes in enough detail to enable penetration pathways to be determined.

- Dark field microscopy of fluorescent dyes, gives pictures of low resolution.

- TEM using dyes containing heavy metal ions gives pictures of high resolution, but they are not so easily interpreted.

Leeder J.D., Rippon J.A., Rothery F.E., and Stapleton I.W. (1985) *Proc. 7th Int. Wool Text. Res. Conf., Tokyo* **V**, 99.
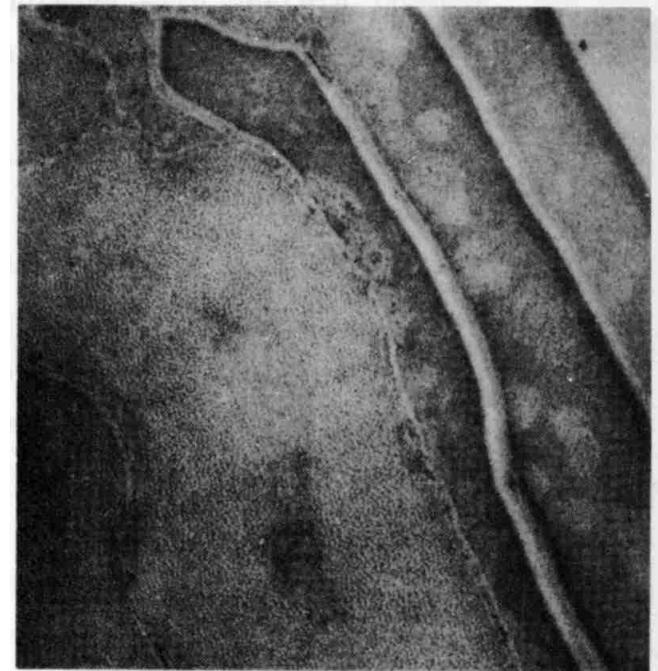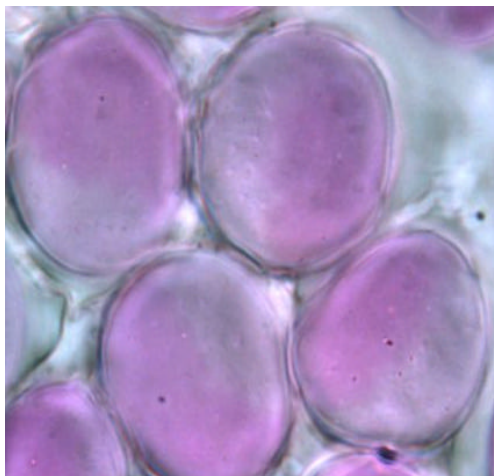

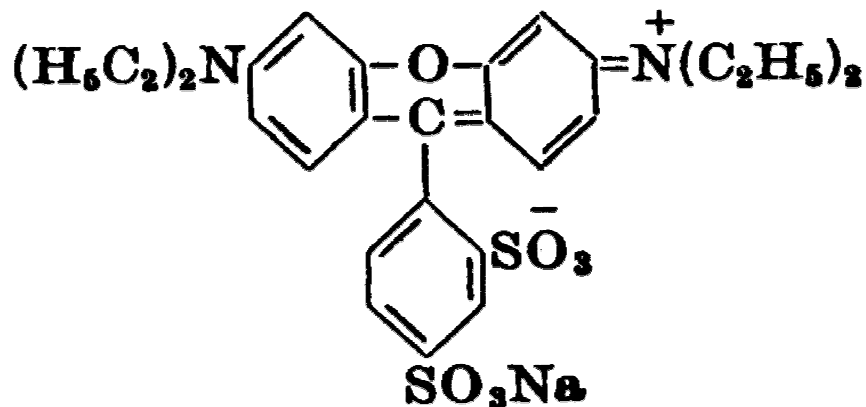Fig. 8. Uranyl dye, 60 min, pH 4.2, 90°C (x 64,000)

A fluorescent dye used to visualise diffusion

The following slides show how fluorescence microscopy can be used to observe the penetration of a dye into Merino wool fibres.

Dyed fibre cross sections in visible light.
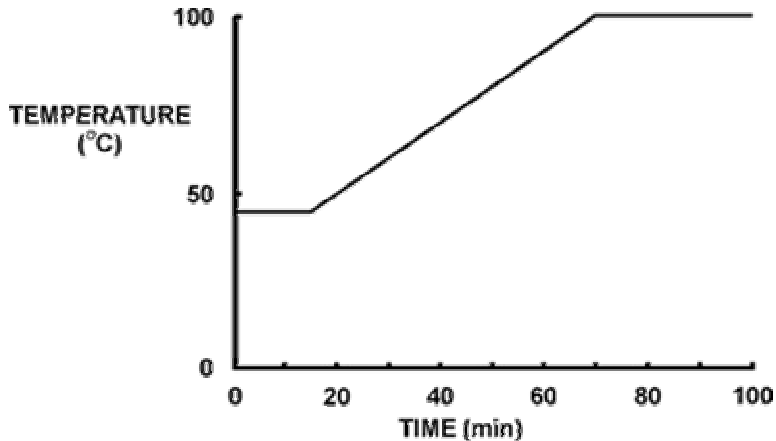
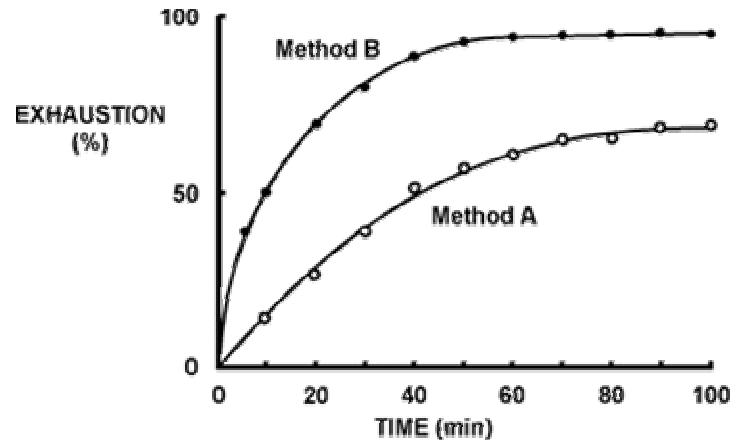The dye used in the experiments.

CI Acid Red 52

Dyeing methods

Method A - no levelling agent
    1% CI Acid Red 52
    10% sodium sulphate
    4% sulphuric acid

Method B – with levelling agent
    1% CI Acid Red 52
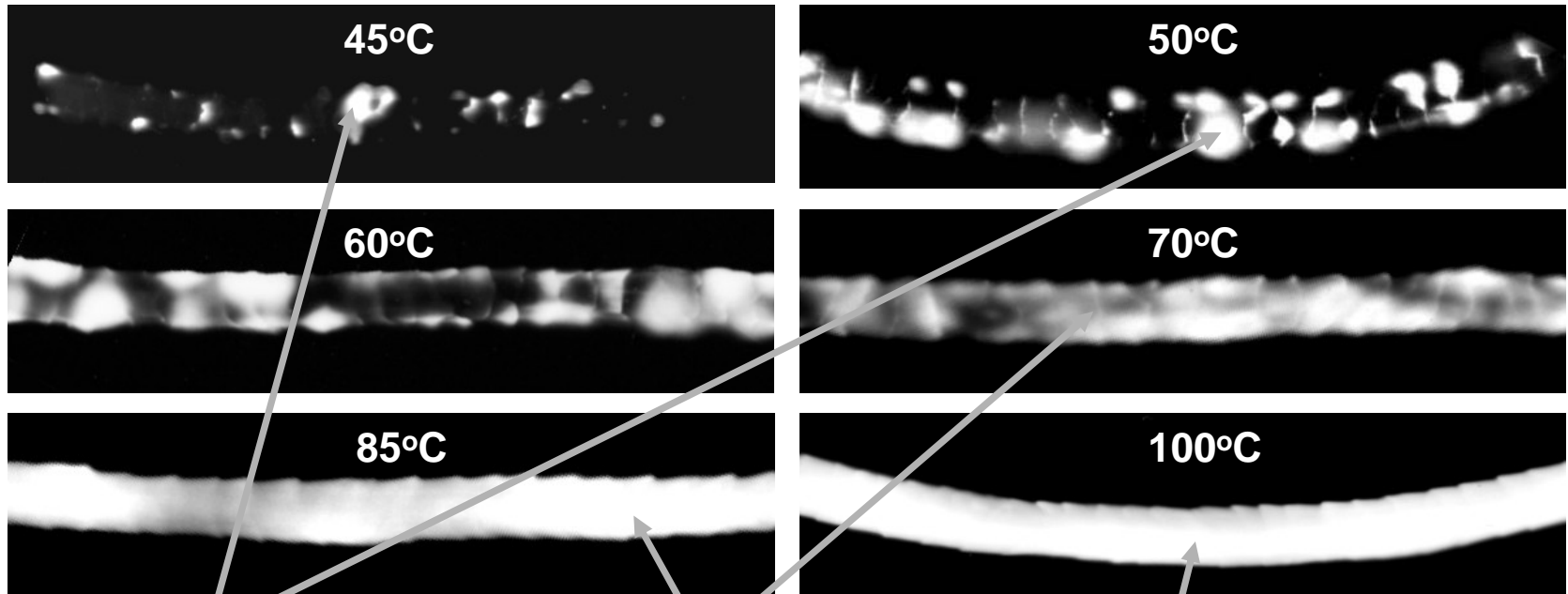   1% Albegal B (Ciba)
    Acetic acid to pH 4.5

Dyeings were carried out in an Ahiba G6B laboratory dyeing machine, at a liquor-to-goods ratio of 70:1.

The fluorescence microscope

Fluorescence is viewed against a dark background.
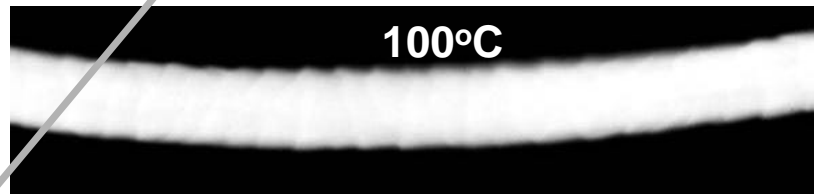
Single fibres – no levelling agent
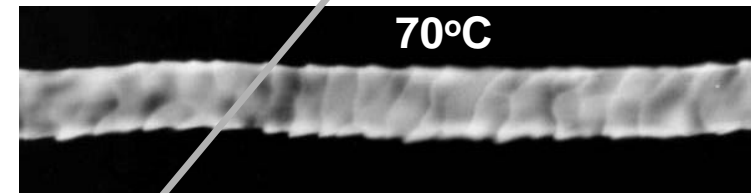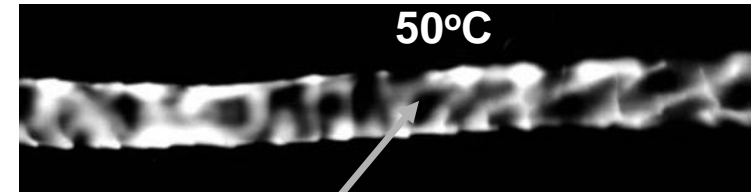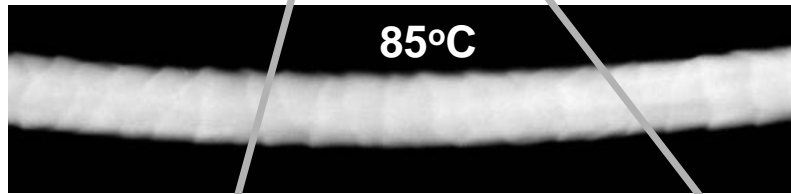

45°C   50°C   60°C   70°C   85°C   100°C

Dye is taken up most readily by damaged parts of the fibre.

Scale edges do not become evenly coloured until the dyeing is well advanced.

The fibres become evenly dyed only near the end of the process.

Single fibres with levelling agent

45°C   50°C

60°C   70°C

85°C   100°C
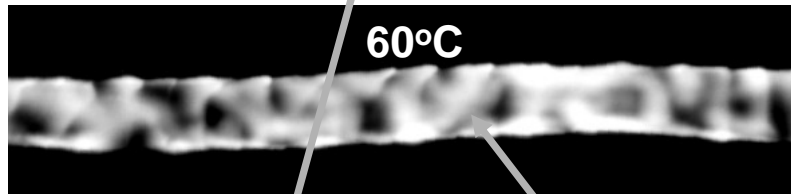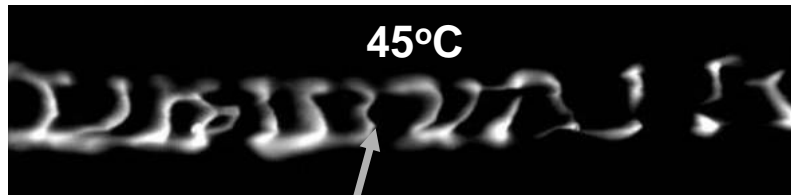
Dye is taken up relatively evenly at the scale edges of the fibre.

Dye appears to migrate from the scale edges and fills in the rest of the fibre.

Dye is relatively evenly distributed along the fibres right from the start of the process.

Fibre longitudinal sections

45°C
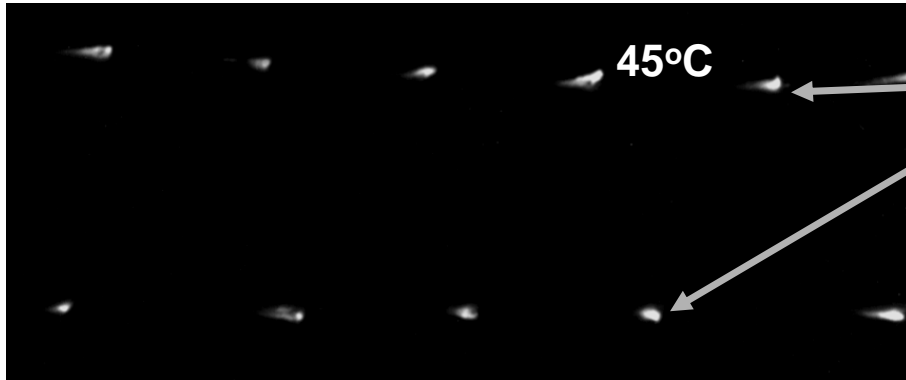
Dye has coloured the ends of the cuticle cells to a similar extent on opposite sides of the fibre.

50°C
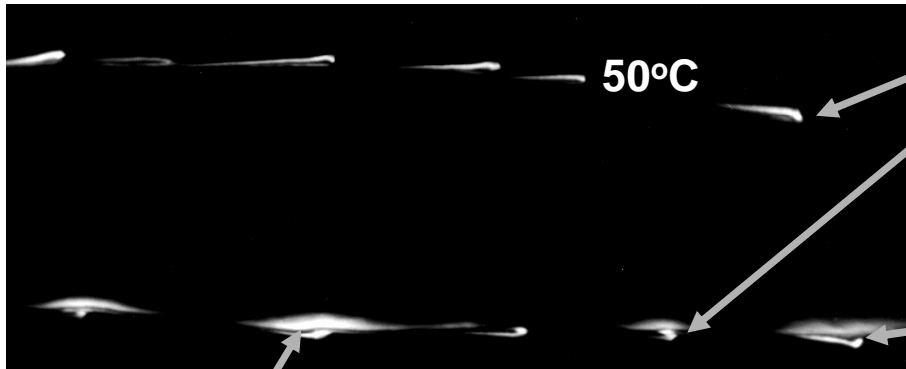
Dye has coloured the ends of the cuticle cells to different extents on opposite sides of the fibre.

Dye is entering one side of the cortex but not the other.

Dye may be diffusing faster in the axial direction than in the radial direction.

Fibre longitudinal sections
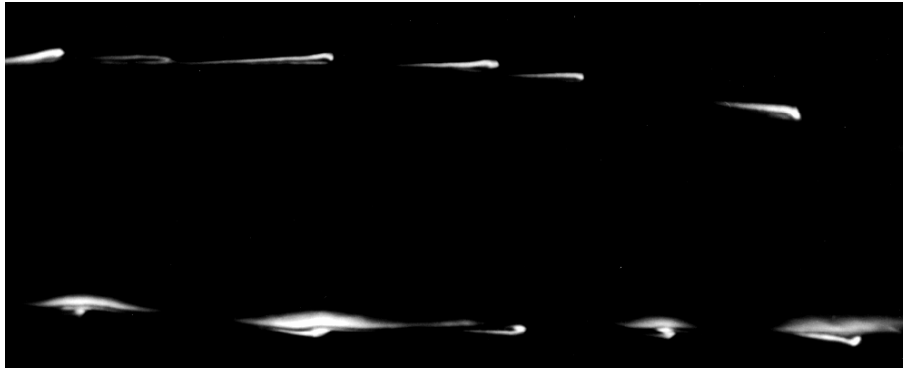
Compare the above picture with this TEM micrograph.

"Le nombre et le recouvrement des cellules cuticulaires ne sont pas les mêmes sur les deux côtés de la fibre, charactérisés par la structure bilatérale du cortex."

P. Kassenbeck, *Bull. Inst. Text. de France* (1946) **76** 7.
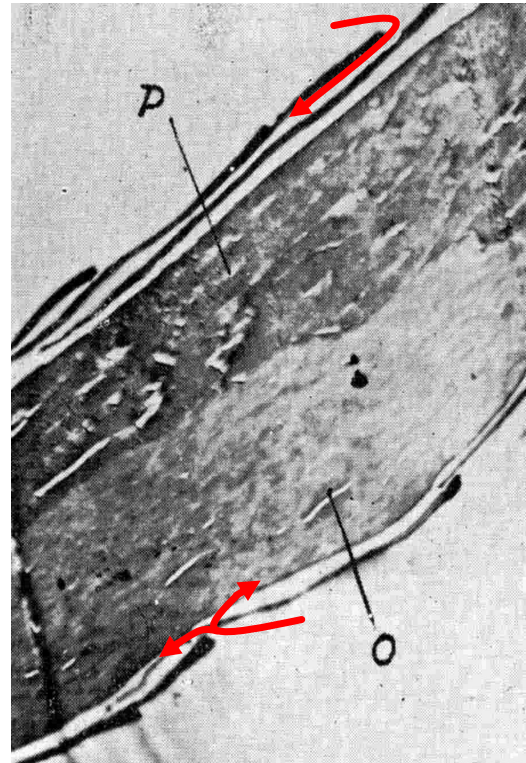
Dye enters the cortex first on the ortho- side of the fibre, because of the shorter diffusion path between the cuticle cells.

A-layer thickness variation
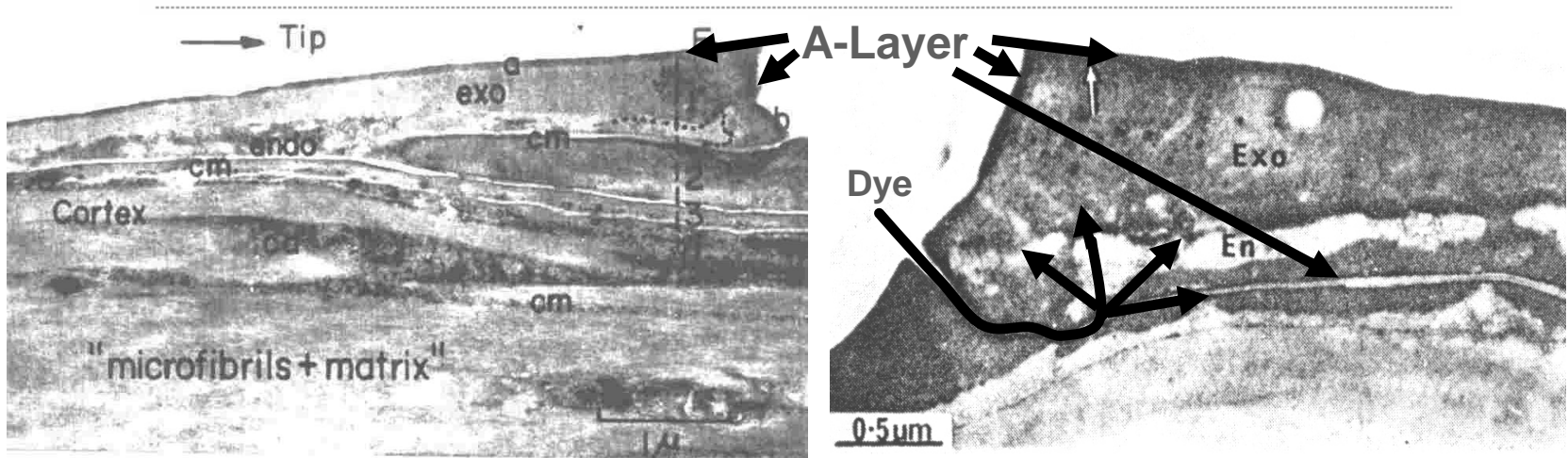
J.H. Bradbury and G.E. Rogers (1963) *Text. Res. J.* <u>33</u> 452.

D.F.G. Orwin (1979) *Fibrous Protiens: Scientific, Industrial and Medical Aspects,* Vol.1, 271.

The dark A-layer extends around the edge of these cuticle cells and becomes thin on the undersides of the cells.
It is most likely that dye penetrates cuticle cells from below.

Dye penetration sequence

45°C 50°C 60°C 70°C 85°C 100°C

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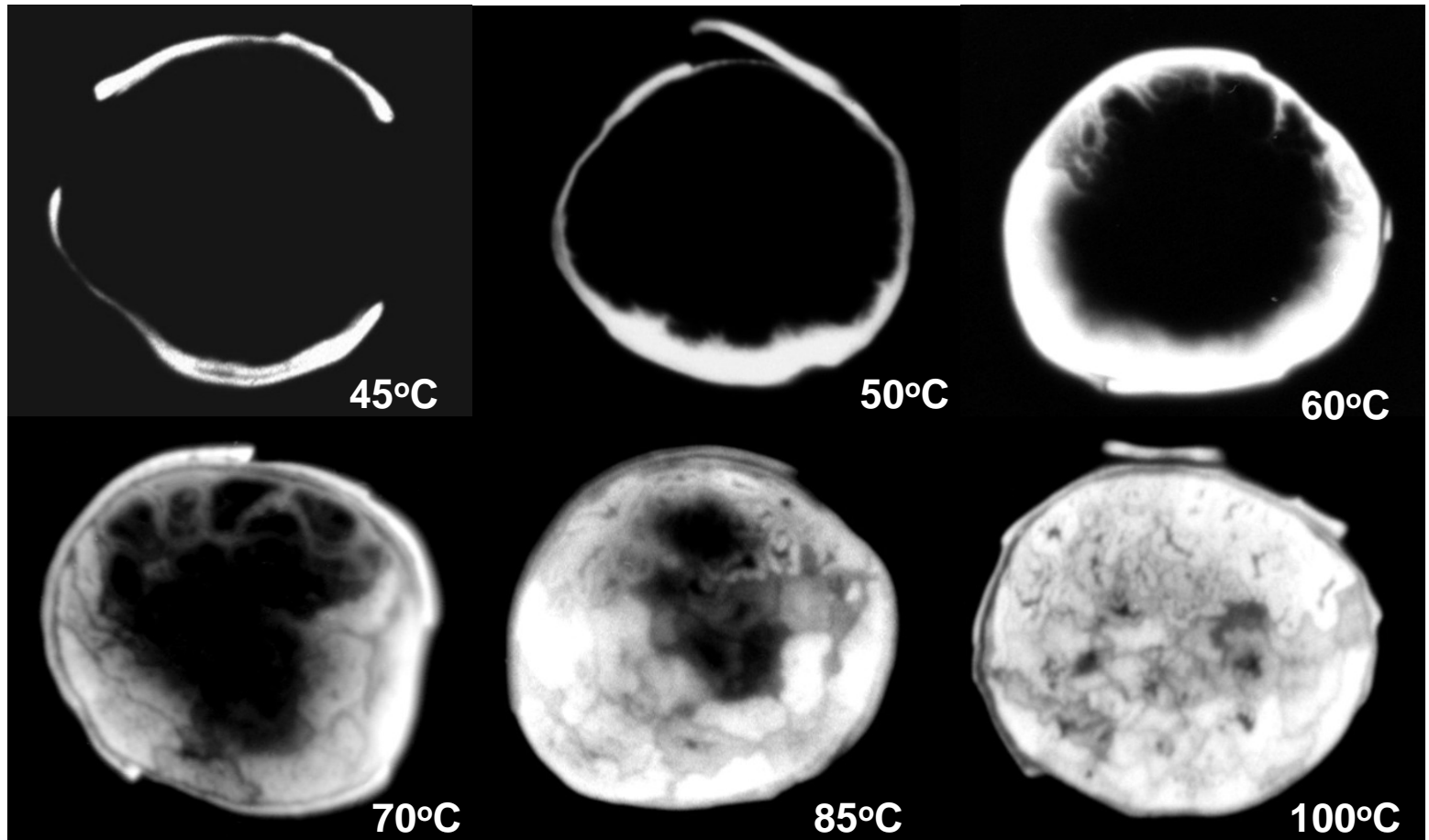
As the dyeing commences
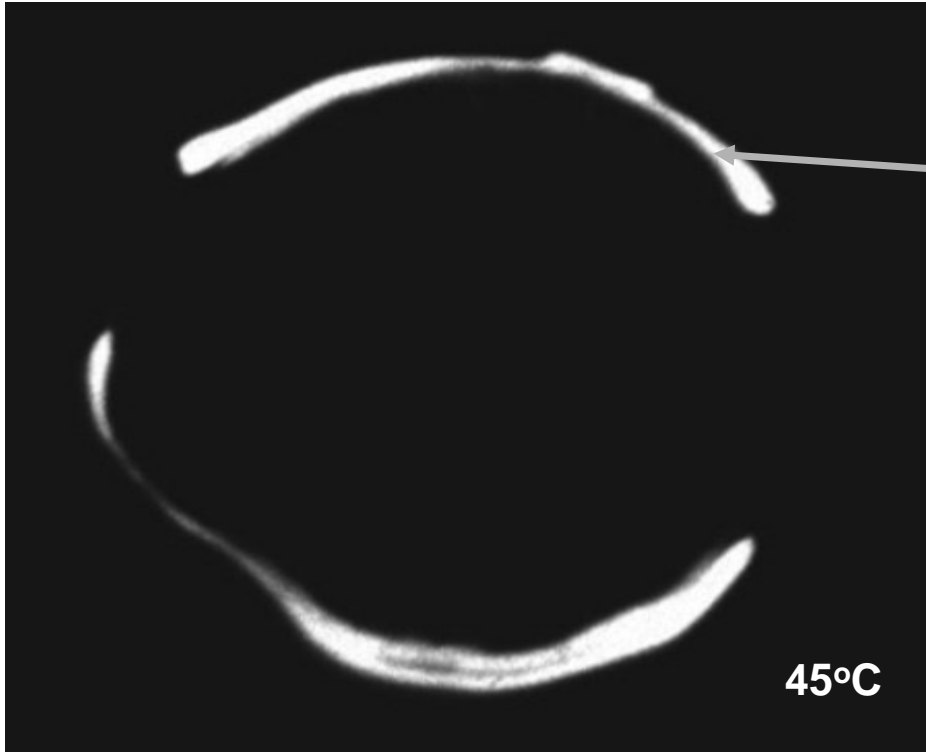
The dye is confined to the cuticle cells.

45ºC

Cross section
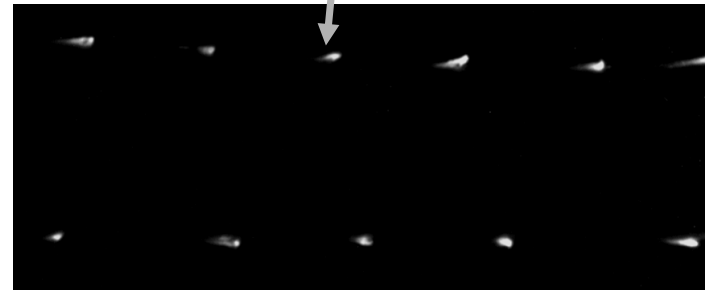
Longitudinal section

Dye begins to enter the cortex

paracortex

orthocortex

50°C
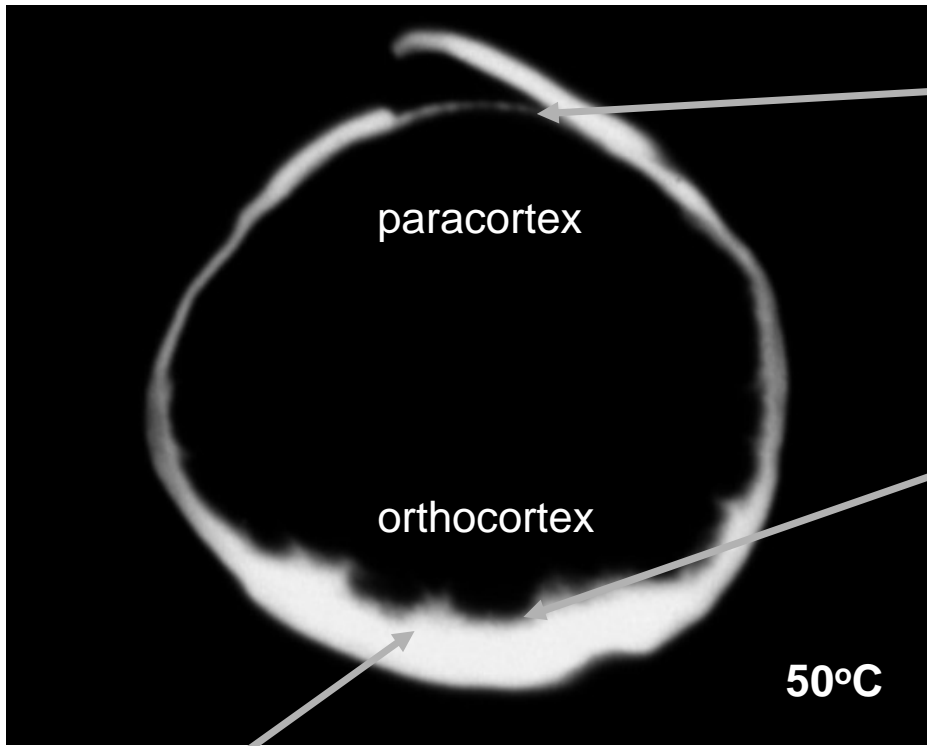
There must be a barrier under the outermost cuticle cell: probably the a-layer of an underlying cell.

Dye is entering the fibre only on the orthocortex side.
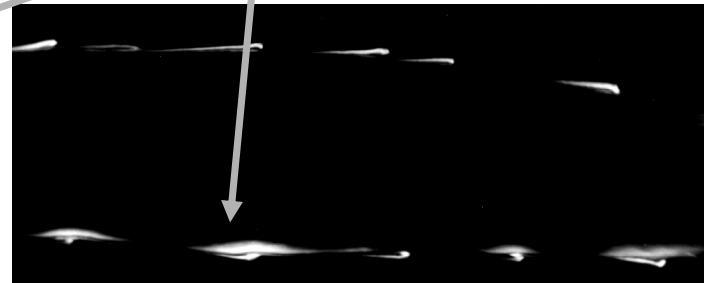
The advancing dye front is uneven because the dye was penetrating the orthocortical cells almost as fast as it could diffuse around them.

Dye is advancing through cortex
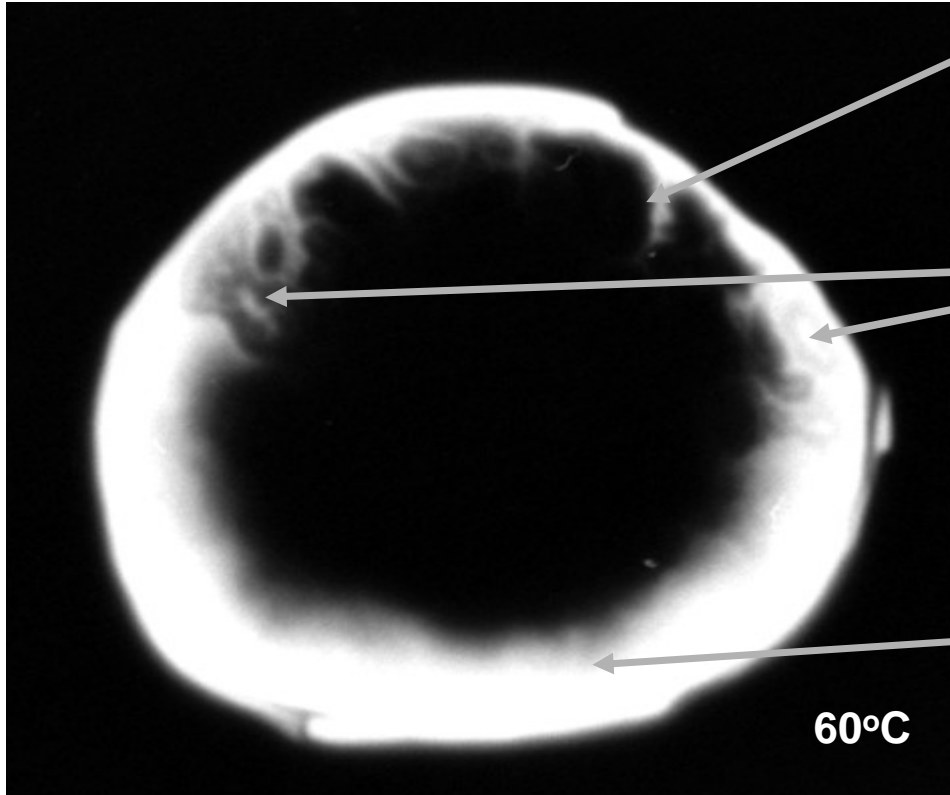
Dye is moving around the paracortical cells.

The nuclear remnants contain dye.

The dye continues to penetrate the orthocortical cells almost as fast as it can diffuse around them.

60°C

Dye is advancing through cortex
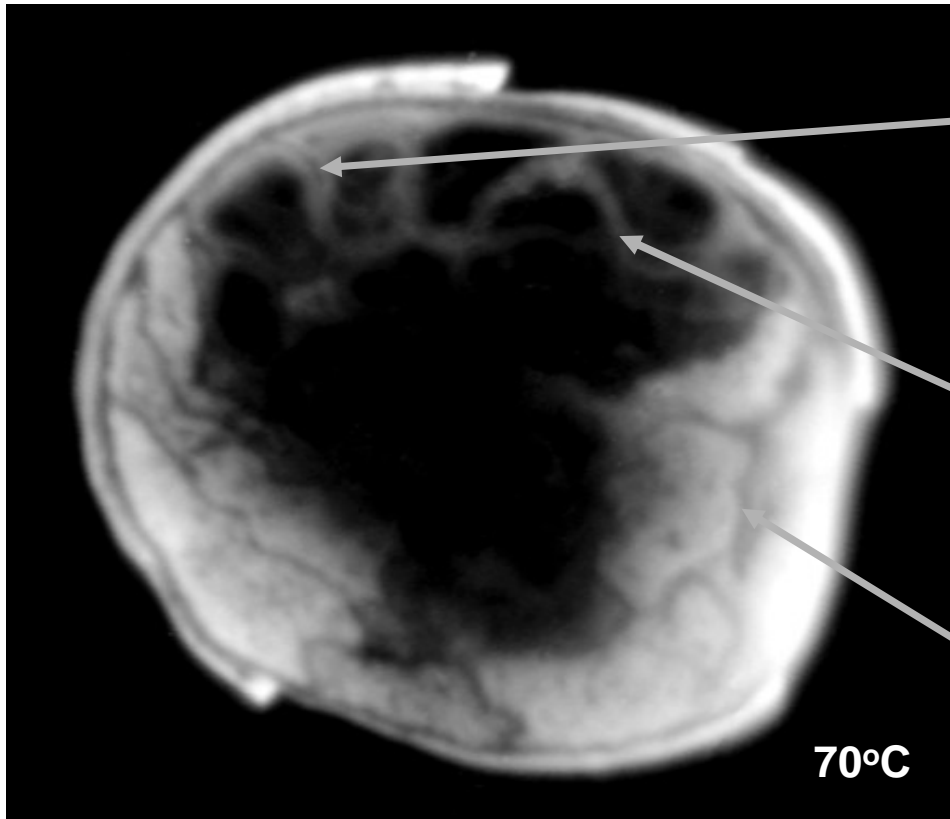
Paracortical cells near the cuticle have dark boundaries.

Paracortical cells are outlined near the diffusion front.

Orthocortical cells have dark boundaries

70°C

Undyed area is off-centre

85°C
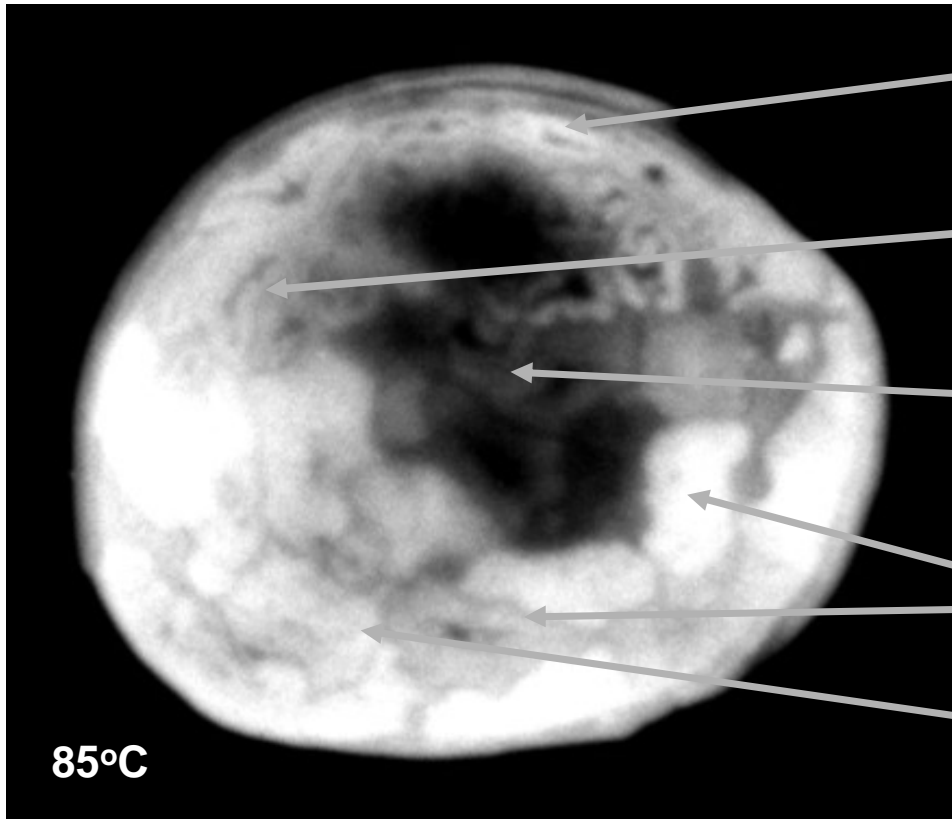
Nuclear remnants are now dark.

Cells have dark boundaries.

Dye has not yet penetrated to the centre of the fibre

Fluorescence varies from cell to cell.

Fluorescence is slightly greater in orthocortical cells.

Dyeing is approaching equilibrium
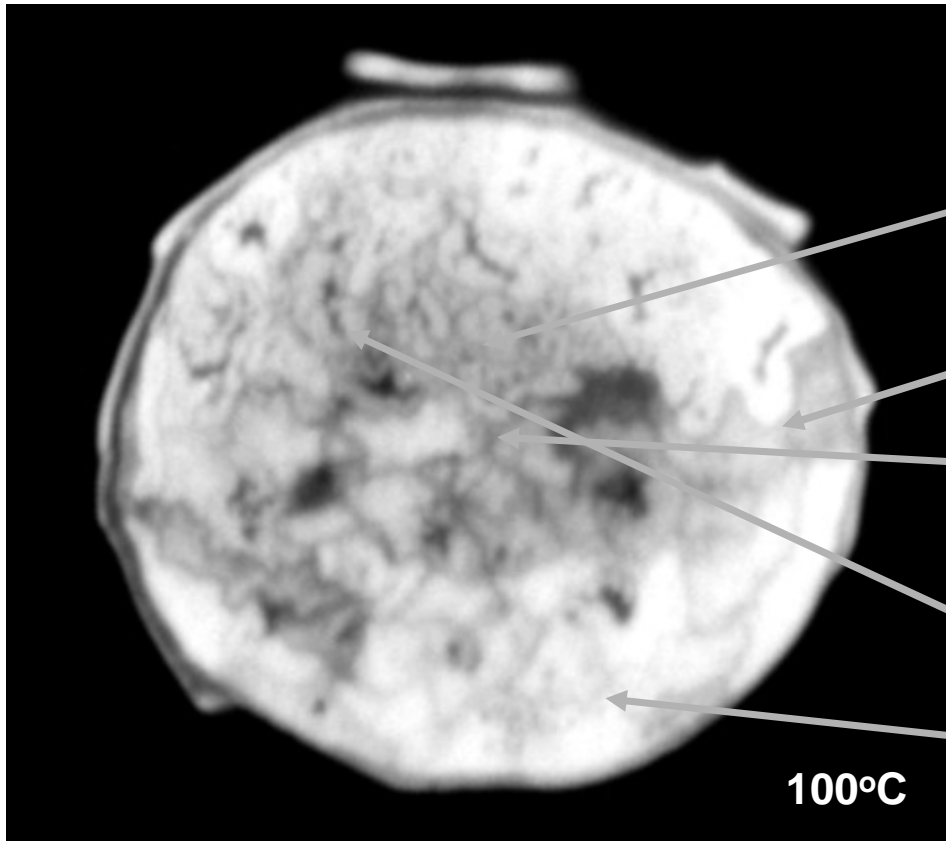
Macrofibrils are brighter than matrix.

All intercellular regions appear dark.

The centre of the fibre is still lighter than the outer regions.

Less fluorescence in paracortex than orthocortex.

100°C

Conclusions about dye diffusion in Merino fibres

- In conventional wool dyeing, intercellular diffusion provides a pathway for the penetration of the dye, with the following qualifications:
    - dye diffusion also occurs rapidly in other non keratinous regions of the fibre, such as the endocuticle and nuclear remnants
    - dye penetrates the orthocortical cells almost as rapidly as it diffuses between the cells
    - dye penetrates paracortical cells more slowly than orthocortical cells.
- At equilibrium, the dye is mostly associated with the keratinous proteins in the cortical and cuticle cells and is no longer in the nuclear remnants and the intercellular regions.

Tippy dyeing

- This term is used to describe unlevel dyeing at the fibre level.
- The tips of the fibres are exposed to sunlight and the cuticle cells become damaged by UV light much more than the sections closer to the root.
- The cuticle cells may break off the fibres and the fibre ends become more hydrophilic and more easily stained by more hydrophilic dyes.
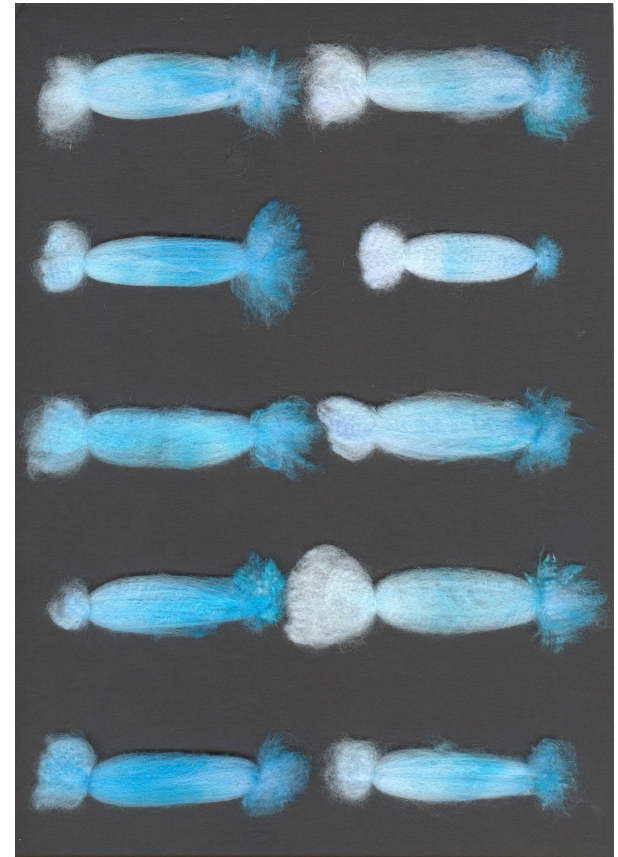
Tippy dyeing

- 'Tippy dyeing' is much more pronounced when dyeing with mixtures of dyes (where variations in hue and/or depth of shade between the tips and the rest of the fibres may occur).
- By selection of suitable dyes and dyeing methods, 'tippy dyeing' can be eliminated or at least minimised.
- Modification of the wool by surface oxidation is also used to overcome tippiness.

Treatments to overcome tippiness

Very deep, even, black and dark blue shades are required, particularly in Japan, for formal and business suits.

- These shades cannot be obtained on wool unless it is treated in some way to modify the cuticle.
- In particular, the lipid layer and the a-layer of the epicuticle need to be removed so that dye can readily penetrate every fibre.
- It is obvious that the treatment must be very even, at both the fibre and macro levels.
- Any treatment which heavily modifies the cuticle is potentially suitable:
  - chlorination with at least 2% of active chlorine is most widely used,
  - soft lustre treatments,
  - vacuum plasma,
  - UV radiation (eg Siroflash).

Fibre structure and dyeing

- The exocuticle acts as barrier to penetration of dyes.
- Damage to exocuticle by weathering during growth leads to tippiness.
- Exocuticle modification is required for maximum colour yields.
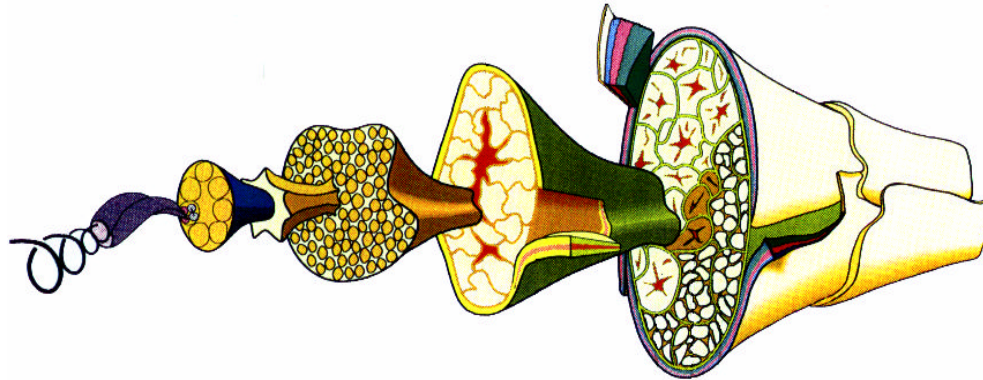
6. Damage during dyeing

Damage to wool during dyeing

- Wool is one of the few fibres that suffers chemical damage during dyeing.
- The chemical damage includes breakage of chemical bonds inside fibres, due to hydrolysis and disulphide bond rearrangement.

Consequences of chemical damage during dyeing

- Fibre breakage in carding and combing increases.
- Yarn and fabric breaking load and extension at break decrease.
- Weaving efficiency is reduced.
- Product range is reduced, specially with articles requiring fine yarns.

Soluble protein

Increases with time of dyeing and 'severity' of dyeing conditions.

- Main soluble fragments have molecular weights of less than 50,000.
- Acid damage gives an increase in fragments with molecular weight less than 35,000.
- Most soluble fragments are low-sulphur proteins.

pH dependence of wool damage
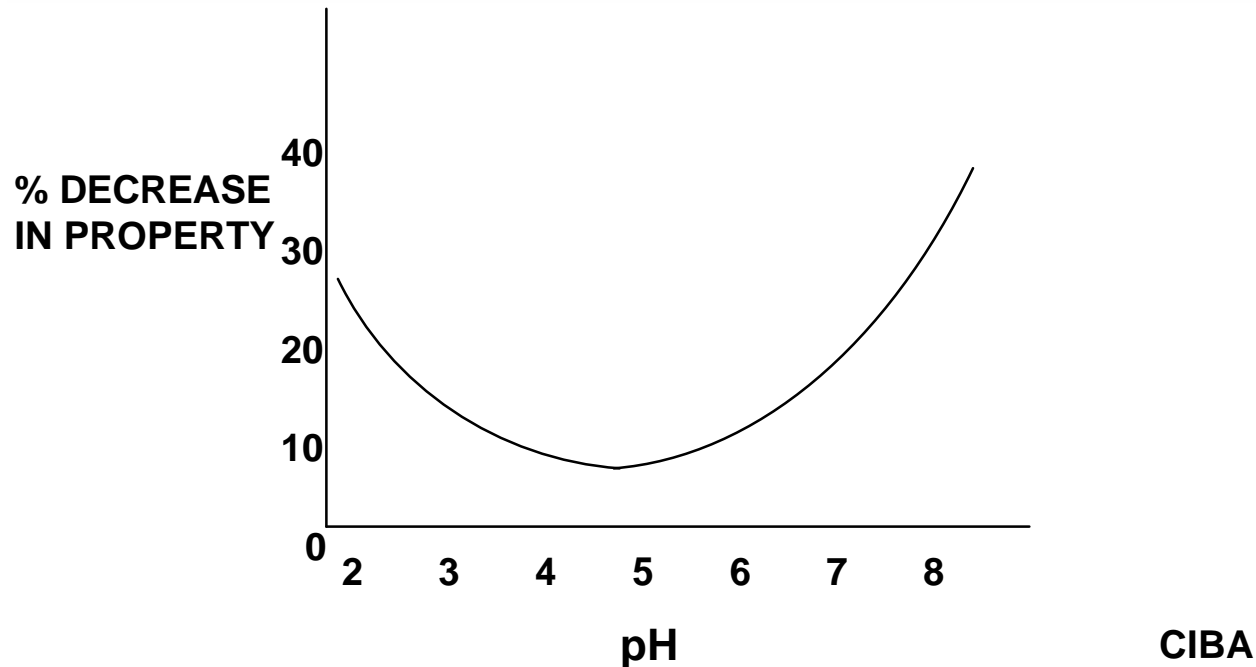
Damage is least around pH 4.8 which close to the isoelectric point where the numbers of negatively and positively charged groups are equal.

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Reactions of keratin in acid solution

- Hydrolysis of peptide bonds, particularly those adjacent to aspartic acid, glycine and serine.
- Hydrolysis of amide side-chains, particularly asparagine and glutamine.
- Acyl shift at serine and threonine.
- Disulphide interchange.

Reactions of keratin in alkaline solution

- Hydrolysis of amide side-chains.
- Hydrolysis of peptide bonds.
- Hydrolysis of disulphide bonds.
- Disulphide interchange.
- Lanthionine formation.

Hydrolysis of polypeptide bonds

$$- \text{CH CO NH CH} - \quad \text{Acid} \quad - \text{CH CO} \quad \text{NH}_3^+ \text{CH} -$$

- CH CO NH CH-
   | |
   R_1 R_2

Acid
®

- CH CO NH_3^+ CH-
  | | + |
  R_1 OH R_2

Alkali
®

- CH CO NH_2 CH-
  | | + |
  R_1 O^- R_2
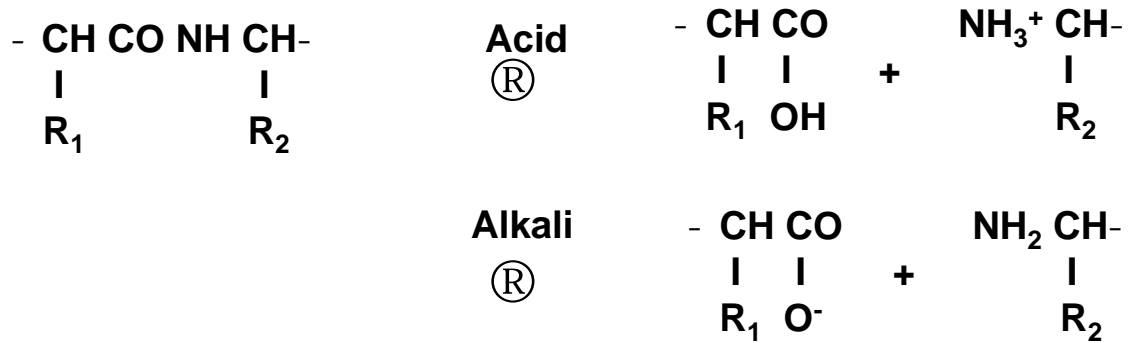
This results in breaking of the polymer chains and consequent weakening of the fibre due to its loss of integrity.

Hydrolysis of disulphide bonds

$-$NH CH CH$_2$ S$-$S CH$_2$ CH CO$-$ **Alkali** $-$NH CH CH$_2$ SS$^-$ CH$_2$ = CCO$-$

| | **®** | + |

$-$CO   NH$-$ $-$CO   NH$-$

       cystene residue   **dehydroalanine residue**

$-$NH CH CH$_2$ S$^-$ +   S

$-$CO

cysteine residue

$-$NH CH = CH$_2$ +   HS$^-$

$-$CO

$-$NH CH CH$_2$ S$^-$ CH$_2$ = CCO$-$ **®** $-$NH CH CH$_2$ S CH$_2$ CH CO$-$

$-$CO   +   NH$-$ $-$CO   NH$-$

                                            lanthionine residue
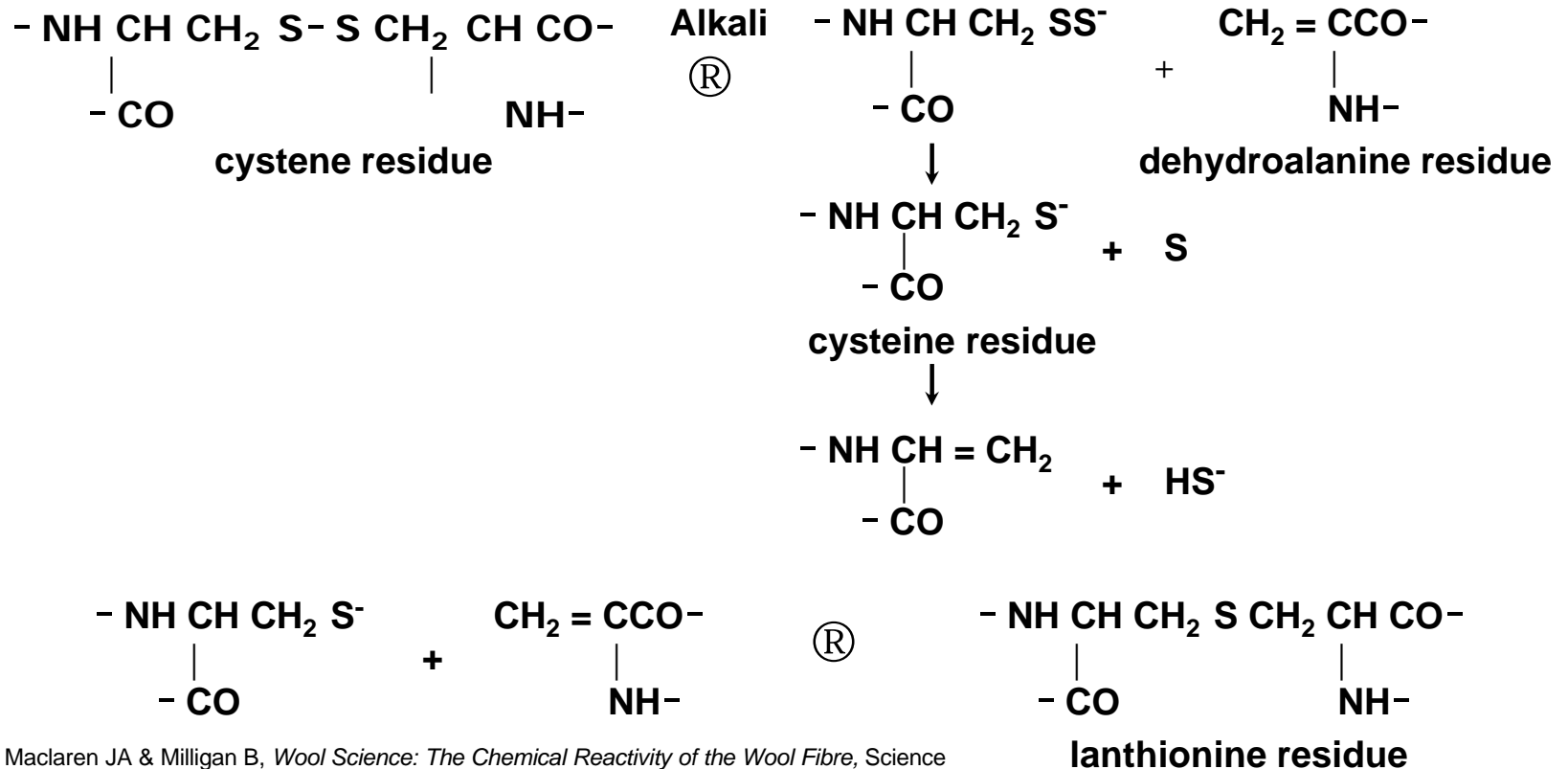
Maclaren JA & Milligan B, *Wool Science: The Chemical Reactivity of the Wool Fibre,* Science Press, Marrickville, Australia (1981).

The role of disulphide bonds in preserving fibre strength

- Hydrolysis of disulphide bonds causes:
  - loss of crosslinking in the matrix which then becomes weaker,
  - fission of bonds that link the microfibrils together which causes major loss of cohesion within the fibres.
- Thiol disulphide interchange in the bonds that link the microfibrils together causes loss of structural integrity.

Rearrangement of disulphide bonds in wool

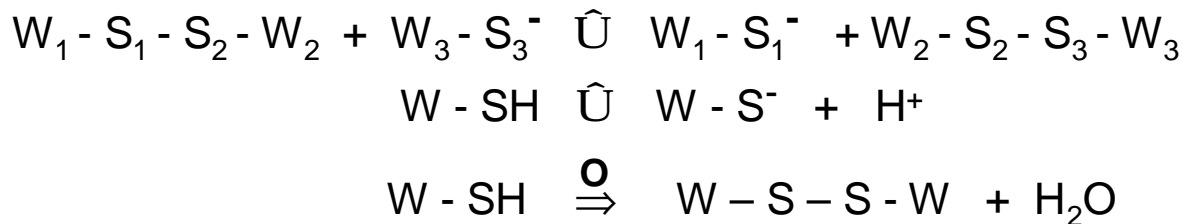- The disulphide bond crosslinks that stabilise the protein matrix and the bonds between microfibrils can be rearranged during dyeing.
- The chemical basis for rearrangement of the disulphide crosslinks is the thiolate-disulphide exchange reaction.

$$W_1 - S_1 - S_2 - W_2 + W_3 - S_3^- \ \hat{U} \ W_1 - S_1^- + W_2 - S_2 - S_3 - W_3$$

$$W - SH \ \hat{U} \ W - S^- + H^+$$

$$W - SH \ \overset{O}{\Rightarrow} \ W - S - S - W + H_2O$$

Subscripts (1-3) have been used to distinguish between different sulphur atoms and the wool polypeptide chains to which they are attached.

- Permanent setting takes place in wool when the disulphide bonds are rearranged. Thus dyeing is also a permanent setting process.

Permanent setting of wool

$$W_1 - S_1 - S_2 - W_2 + W_3 - S_3^- \quad \hat{U} \quad W_1 - S_1^- + W_2 - S_2 - S_3 - W_3$$

$$W - SH \quad \hat{U} \quad W - S^- + H^+$$
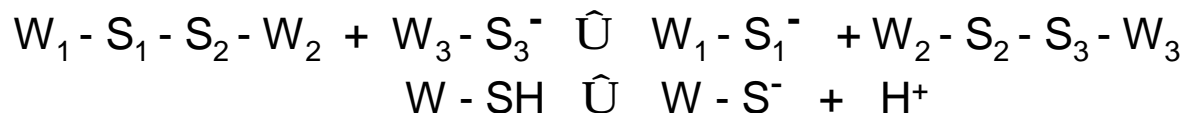
- The thiolate/disulphide exchange reaction depends on the presence of small amounts of cysteine in wool.
- The thiolate ion concentration can vary with the previous history of the wool and the pH of the fabric.
- The rate at which the disulphide bonds rearrange depends on the temperature and the thiolate ion concentration. The pH affects the equilibrium between thiol and thiolate ions in the wool.
- The rate of setting increases with pH, as the thiolate concentration in the wool increases.
- The thiolate/disulphide exchange reaction can be frustrated if the thiolate concentration can be kept very low by the presence of an 'anti-setting agent' that can react with free thiol or thiolate groups.

$$W - SH + ASA \quad \hat{U} \quad W – S- ASA$$

Methods for measuring chemical damage

- Alkali solubility.
- Urea/bisulphite solubility.
- Soluble protein.
- Wet bundle strength for fibres.
- Wet bursting strength for fabrics.

Alkali solubility test

- The method measures the amount of wool that dissolves in 0.1M NaOH solution @ 65°C for 1h (BS3568).
- Solubility increases with:
  - peptide bond cleavage,
  - disulphide bond cleavage.
- Solubility decreases with formation of alkali-resistant crosslinks.
- Increase does not always correlate with decreases in mechanical properties.

Urea/bisulphite solubility test

- The method is similar to the alkali solubility test except the solution used is a mixture of urea, sodium bisulphite and sodium hydroxide (BS3584).
- The solubility of wool in this test provides information on the change in chemical properties as a result of chemical treatments.
- When wool is treated in neutral or alkaline solution, or steamed under neutral or alkaline conditions, solubility usually decreases.
- Hence the method is particularly useful for investigating setting processes.
- Dry heating or treatment with cross-linking agents also causes decreases in solubility.
- Solubility decreases with the formation of lanthionine from disulphide bonds by alkali hydrolysis.
- Oxidation or dyeing under acid conditions increases the solubility.

Methods of protecting wool from damage during dyeing

- Dye close to the isoelectric pH.
- Use temperatures below the boil, if possible, to reduce protein hydrolysis.
- Use anti-setting technology to inhibit thiolate/disulphide reactions in wool during dyeing.
- Use reactive dyes.
- Above the boil, introduce crosslinks with formaldehyde-based products to replace broken amide and disulphide crosslinks, (these products may not be acceptable because of health regulations).
- Protein hydrolysates have been recommended are they are not as effective as the above methods.