Dyeing methods for wool

Mr Arthur Fisher

CSIRO

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Introduction

The physical structure and chemical constitution of the wool fibre

Over many years, research workers have acquired a very intimate knowledge of the physical structure and chemical constitution of the wool fibre, and a brief outline of some of these properties will be given here.

Like other animal hairs and fibres, wool is an extremely complex structure consisting of keratinous cells containing fibrils, matrix, modified cell membranes and remnants of cytoplasm.

Approximately 80 per cent of the weight of the fibre is due to different types of keratin substances. The fibre consists of a number of different physical phases and is a much more complex structure than the synthetic or man-made fibres, and thus requires much more detailed attention during dyeing and finishing processes.

The outside surface of the fibre, which is the scaly covering, is the cuticle and beneath this is the cortex or the fibre core. The cortex is made up of keratin containing cigar-shaped cells and cytoplasmic and nuclear remnants surrounded by a cell membrane complex. The keratin is aggregated into macro-fibrils and within these a micro-fibril/matrix complex is present. The micro-fibrils are made up of proteins in an alpha-helix configuration surrounded by an amorphous cystine-rich matrix.

When dyeing and finishing wool it must be remembered that there are many variables to be considered and that the physical and chemical nature of the fibre may be dependent on the breed of animal, climatic conditions, type and quality of feed and prior processing of the fibre before finishing.

Wool is a protein fibre and its chemistry is characterised by its amino acid content and the types of side chains it contains. Both of these control the effects that acids, alkalis, oxidising and reducing agents have on the fibre.

From a dyeing and finishing perspective, the most important chemistry of wool revolves around the following types of groups:

- disulphide bonds

- end groups and peptide groups of the protein chains

- side-chains originating from amino acids.

The disulphide bonds in the wool fibre are very important from a finisher's point of view. These are covalent cross-links, which can be broken and re-formed and play an integral role in wool fabric finishing because of their importance in fabric setting.

Wool contains ammonium groups together with carboxylate groups at the isoelectric point. When dyeing with acid dyes some of the carboxylate groups are un-ionised and the dye anions are attracted by the positively charged ammonium groups.

Electron micrograph of a Merino wool fibre.

INTERCELLULAR
DIFFUSION

TRANSCELLULAR
DIFFUSION

epicuticle

exocuticle 'A'

exocuticle 'B'

endocuticle

intercellular cement
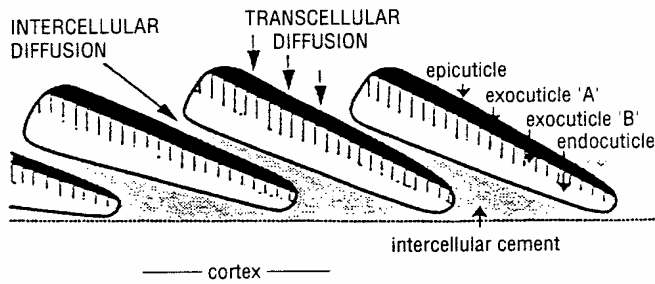
cortex

Alternative pathways for diffusion into the wool fibre

1 2 3 4 5 6 5 7
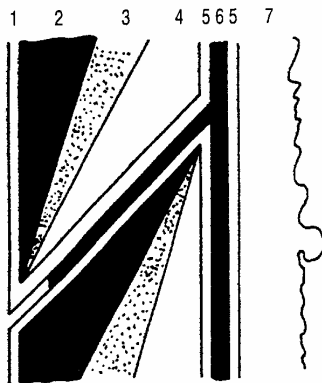
Model of the surface barrier (cuticle) for diffusion processes
1. *epicuticle*   2. *exocuticle*   3. *mesocuticle*
4. *endocuticle*   5. *cell membrane complex*
6. *inter-cellular cement*   7. *cortex*

Fine structure of macrofibrils in wool fibres.

Contemporary wool dyeing and finishing
Dyeing methods for wool: Arthur Fisher

keratin

IFAP

interfilament
material

right-hand   dimer   sub-filament   filament   macrofibril
a-helix

1   2   3   7   200 nm
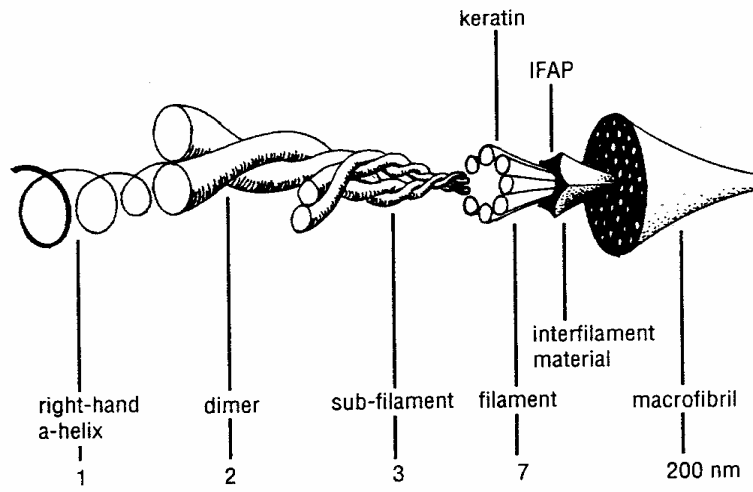
1.   The history of dyeing

1.1   Prehistorical use of colour

It is generally accepted that the earliest use of colour by *Homo sapiens* was discovered in the cave art of Cro-Magnon men of 15,000 years ago. The caves at Altamira in Spain and at Lascaux in France almost exclusively used mineral pigments of red, brown, yellow, black and white to depict bison, horses, reindeer and other animals. At this stage, blue and green were unknown.

In the Neolithic period, from 7000 to 2000 BC, the technological expertise for spinning and weaving had been developed. Dyeing was an obvious extension of this. Samples of textiles from central European lake villages dating from 4000 to 3000 BC used blue, red, lilac and yellow from plant sources. Obviously, these colours can give rise to many others.

One widely used natural colouring was woad (a vegetable extract), also used for decorating bodies. Although it required a complex series of processes to extract woad from its plant source, it appears in many cultures about this time. The ability to perform such processes infers that many other less complicated dyes were also in use by the time mankind reached the Bronze Age. The colouring method of woad is the same as that for indigo, which is a vat dye still used today, although mostly produced synthetically. Primitive peoples today still use colourants of vegetable origin to produce blacks, browns, reds, yellows and blues to decorate themselves and their textiles.

The spread of dyeing technology and commerce was widespread by 800 BC. Buried with the remains of a queen in Sweden at that time were weaving implements and quantities of plants used for dyeing. These included woad and madder. Madder is an important natural source of the red dye alizarine, whose derivatives are still in use today. However, it must have been sold to the northern people, as it could not be cultivated at those latitudes.

With the arrival of the Iron Age, the use of iron derivatives further developed the possibilities of colour.

1.2   Dyeing processes in ancient civilisations

While Europe was progressing to the Iron Age, the great civilisations of the valleys of the Nile, Tigris, Euphrates, Indus and Yellow Rivers had developed textiles and the ability to colour them using dyeing processes.

In Eygpt, the dynastic period began in 3200 BC, that is, when historical records began. Apart from ochre and lampblack pigments, organic materials (that is, those obtained from plants) such as henna, saffron, woad, indigo and madder were used. There is also evidence of alum being used to 'mordant' or 'fix' the dyes more permanently to the textiles once the dye was applied. Indeed, without mordanting, the organic materials generally had poor fastness properties. Mordants do not have to be used for the majority of modern dyes, but the practice of after-treating the dyeing with other chemicals to improve the fastness still appears in many cases.

The Egyptians also had access to natural sources of sodium carbonate (washing soda) which when mixed with artesian clays was important in the bleaching of linen, the prevalent fibre of that time. They were also aware from experimentation of the properties of many metallic oxides, some of which could be used to colour textiles, for example, copper salts can give greens.

Between the Tigris and Euphrates Rivers lay Mesopotamia and Chaldea. The biblical stories of the Assyrians, Babylonians, Persians, Phoenicians and, of course the Hebrews,

show that trading in fabrics and dyes was commonplace. Although Egypt was an important linen producing country, Mesopotamia was a wool producing country and, hence, each developed different techniques in dyeing

Reds were produced from muscats, as madder was not known in Mesopotamia, yellow from pomegranates, and yellow-browns from sumac. Reds were particularly popular, but records exist of violet, red-brown, and golden yellow shades.

In Mesopotamia, the wool was dyed in fleece form, whereas in Egypt linen was dyed as yarn before weaving.

Archaeological evidence shows that spinning, weaving and dyeing was concentrated in certain cities in Israel, particularly along the coast. Hyacinth, purple and scarlets, were common shades. Black dyes were produced from tannins of oak galls, and from bitumen.

As with Egyptian dyeing, a mordant was necessary to get adequate fastness properties, and alum was the most important of these. The purple and hyacinth used by the Hebrews were imported from Phoenicia, and were so noted for brilliance that the region was renowned throughout the ancient world for its 'purple'. The dye comes from molluscs of the genus Murex and Purpura. It is applied in a similar way to indigo; that is, it must be reduced and then applied to the fibre before reoxidation. Tyrian purple was a very bright red produced by successive dyeing with extractions from two different molluscs. The process was very expensive, requiring thousands of shells to provide small amounts of colourant. High dignitaries regarded purple garments as a symbol of power and authority.

The Phoenicians were also skilled in simulating the shades of the expensive purples with cheaper materials. They collected materials for their processes from many foreign areas visited by their merchant ships. Their techniques were secret and carefully guarded, although over the centuries they did leak out to the Greeks, Romans and Byzantines.

The Persians developed many shades for use in their carpets. Madder extracts were fermented to produce rose reds and indigo fermented for turquoise tones. Many yellows were available from plants. The speciality of the Persians was scarlet derived from the female of an insect which lives on the kermes oak. This scarlet was a standard for reds until synthetic dyes appeared. The shade of the material extracted varies from orange to purple, depending on whether it is under acid or alkaline conditions, or treated with salts

In India, dyers were familiar with indigo and used betel in a similar way to the henna of the Egyptians and Middle Eastern countries. Madder was also known. Many mineral colours were also used, although more for printing than dyeing. Cotton was the most important fibre.

The Chinese applied their skills to silk as well as the more common fibres. It is thought that they had well established techniques for the dyeing of a range of shades on silk some 4000 years ago.

The 'Lan' plant was used for yellows and safflower for reds. Indigo was known, and could be modified with selected yellows, and a particularly expensive green could be produced by a long, complicated process using parts of the Rhummus plants.

Blacks were also produced. The Chinese knowledge was very carefully guarded. It was gradually modified by new materials and techniques filtering in from India and Persia, resulting in a magnificent range of hues being produced. The eventual importance of the Silk Road to Europe was partly a result of their skills in producing a very desirable item.

Quite independently, the Central American civilisation of the same time had developed dyeing techniques for wool and cotton which used indigo, reds similar to madder, which was not native to the New World, as well as the cochineal insect for red. Mordanting with alum and iron was also used. The technology used is similar to that of the present Araucans

of Chile, who are able to obtain a full range of shades, except in the blue area, from plant extracts available to them locally.

The 'purple' process of the Phoenicians was also known to the Mayans, and similar processes are still used in native cultures of the region.

1.3   The Classical period

The time of Greek and Roman dominance, from 600 BC to 400 AD, was one during which the trading activities of the Phoenicians and their successors continued.

The dyes and techniques used were principally those of the Middle East civilisations already mentioned. The period was one of conciliation rather than the development of new techniques. New plant sources were introduced from the northern and western parts of Europe, as the tribes of those regions also had adequate ranges of shades, although limited compared to those of the Romans in particular. Rome's role was to spread this knowledge throughout its empire.

Techniques acquired included new ways of dyeing purples from the Gauls and green from the northern tribes directly from Juniper, rather than overlaying woad with a yellow.

1.4   The Middle Ages

The Middle Ages were again a static period in the development of dyeing in Europe. The principal event was the introduction of silk, which being delicate required much more care than the traditional fibres to date. This resulted in a refinement of technique, and a codification and control of products used by dyers, particularly in Venice, in order to protect the reputation of their products.

By the 14th century, corporations and guilds had been formed to continue the dyer's art, which was essentially still based on the old Mediterranean techniques.

1.5   The Renaissance and the 17th century

The Renaissance period was yet another which did not see great technical advances, but had a significant impact because of the development of the printing press. The information previously closely guarded by the dyer became available to the literate. The most famous of these books is the *Plithco* of Rosetti, which was printed in Venice in 1540. This gave methods of dyeing wool, cotton, and linen, silk, leather and furs.

Another factor was the opening of trade with the New World and new, faster sea routes with the East, which avoided the dangerous overland routes. With many middle-men in the trade chain, indigo became readily available from both directions, and replaced woad.

Logwood was introduced from the Caribbean for blacks, and is still occasionally used today. Other new dyes extracted from the vegetation of the New World were also introduced. Cochineal became an important colourant in the European dyer's inventory.

However, during the 17th century the sciences began to bring new understandings of acids, bases and salts. Science began to intrude into the dyer's workshop and explored the use of a wide range of metal salts as mordants.

Until this stage, each dye had its own particular techniques for application. Shade matching as such was not common because cross-compatibility of dyes and methods was low.

1.6   The 18th and early 19th centuries

It is true that with the notable exceptions of metallurgy and glass making, the applied chemistry of the time was essentially that of the art of dyeing. Further systematic exploration of the application and fastness properties of dyes and the influence of chemicals on them, was the dominant theme of chemists.

One important 'discovery' not recognised at the time was the production of aniline by treating indigo with quicklime. A hundred years later, aniline would be an important starting point for the manufacture of many other dyes.

The scientific approach to mordants also resulted in new colours and properties from the traditional dyes. The fibres and fabrics themselves could be transformed by new chlorine bleaching processes before dyeing was done, also increasing brightness and fastness.

The Napoleonic wars of the early 19th century cut France off from the raw materials required by dyers from the Americas and the East. The French chemists responded to a challenge to find adequate substitutes for these.

However, it was not until the mid-19th century that scientists began to go beyond the colours provided by nature, apart from simple modifications of the natural colours.

1.7   The development of synthetic dyes

1.7.1   Early discoveries

Tentative approaches began late in the 18th century, but their basis was not clearly understood. Woulfe in 1771 had treated indigo with nitric acid and dyed wool and silk with the resultant yellow colour, which we know as purpuric acid. Scheele in 1776 obtained purpuric acid by treating uric acid with nitric acid, and obtained a reddish residue with colouring properties after evaporation.

Proust prepared the aniononium derivative of purpuric acid in 1818 and Runge in 1834 oxidised crude phenol and produced rosolic acid.

All of these substances dissolved readily in water and dyed animal fibres easily, but were little more than extensions of the traditional empirical searches the dyer had pursued for centuries.

However, by the 1840s Van Troffman began a systematic exploration of tar products left after the generation of coal gas. Runge had isolated aniline from woad tars in 1834, but Hoffman developed a method of producing it by the reduction of nitrobenzene, and began to look at other derivatives of it.

1.7.2   Perkin's breakthrough

Perkin, the discoverer of the first artificial dye, was a student of Hoffman. In 1853, he was attempting to make quinine by oxidising aniline derivatives, but only succeeded in making a dark mass. However, on treatment with hot water, it partly dissolved and formed a purple solution from which violet crystals could be prepared. He found that these would dye silk a magnificent purple shade, which had good fastness properties and brightness. This 'mauveine' was the first link in a vast network that developed.

Perkin borrowed money from his father and began producing mauveine, but first had to develop appropriate methods for the production of industrial quantities of nitrobenzene and hence aniline of sufficient purity. Perkin's success encouraged others to explore the coal tar products.

In 1859 in France, Verguin discovered fuchsin after heating aniline to high temperatures in the presence of metallic chloride. Fuchsin was even more beautiful and brilliant than mauveine, and had an immediate impact on the market. Experimentation by other chemists soon resulted in cheaper alternative methods for the production of fuchsin.

Before long, violets, blues and greens were synthetically produced, but although brilliant and easy to apply, the fastness was not always good, and vested interests in supplies of natural materials did not cause their use to be encouraged.

The reputation of poor fastness dyes which aniline dyes had was countered in part in 1860 when greens and blacks were produced by applying aniline to cotton and oxidising it on the cotton. This procedure is still in use today to produce aniline blacks.

1.7.3   Industrialisation

Many of the great dye firms of today came into existence in response to the opportunities evident: Durand and Heugenin in 1862, Ciba in 1873, Gelgy in 1864, and Sandoz in 1886. Perkin's tutor, Hoffman, was persuaded to return to Germany and with Kekule made a significant contribution to the education of German chemists. BASF was formed in 1865, and in that firm, the synthesis of the two principal natural dyes, alizarine and indigo, eventually were developed. Bayer had begun in 1861, and by 1865 opened their first factory in the United States. Hoechst and Cassella were also founded in this period.

1.7.4   Synthetic production of alizarin

It was really the theoretical work of Kekule which gave the Swiss and German chemists a systematic approach to the synthesis of organic aromatic chemicals. It was this knowledge that allowed Graeke and Liberman to determine the structure of alizarin, the chief colourant in madder root. Within a year they had produced alizarin synthetically. Alizarin was the first synthetic dye which was exceptionally fast to washing and light. By 1870 the madder industry in France was destroyed, and before long the competition had reduced the price of synthetic alizarin to a tenth of its original price.

Alizarin type dyes, based on anthraquinone derivatives were produced in a wide variety of shades. They not only replaced the natural mordant colours, but created new shades and fastnesses. Their use on cotton was simplified by the use of sulphonated oils.

1.7.5   Azo dyes

In 1862, the first azo dye was produced from the treatment of metaphenylene diamine with nitric acid. This was known as Bismark Brown, and was the first member of the largest class of dyes now in use. It was however the only one of its type for quite some time until its structure was understood in the light of Kekule's theory. In 1876 the first of the sulphonated azo acid dyes for use on wool and silk appeared. The Swiss soon developed a scarlet dye with two azo groups which rivalled and soon replaced the natural cochineal colour.

In 1887 the first azo mordant dye, Alizarin Yellow GG was produced, that with a chromium mordant, soon replaced all natural yellow dyes.

1.7.6   Direct dyes; synthetic indigo

However, most of the discoveries to this time were mainly associated with wool and silk dyeing. Cotton still required natural dyes for most shades. In 1883, the Geigy laboratories produced Sun Yellow which could be applied directly to cotton.

This was the first of the 'direct' dyes, and was followed in the next year by Congo Red, the first of the substantive cotton dyes.

Before long, a wide range of shades had been developed. Natural dyes become less important, with the exception of indigo. Its formula had been determined in 1868, but it was not synthesised until 1880, and was too expensive to produce commercially. Huge efforts and finance were applied to developing commercially viable manufacturing by BASF, and resulted in the first pure indigo being placed on the market in 1897. It became the first of a range of indigoid vat dyes.

1.7.7 Sulphur dyes: azoic dyes: vat dyes

Sulphur dyes had been used unknowingly in France since 1873, because fast shades could be produced on cotton by treating it with alkaline reducing residues of natural dye woods, and then oxidising them. Twenty years later, the first sulphur black was manufactured', and because of their low cost and simplicity of application, similar blacks are still in use today. Many other sulphur dyes were developed by the end of the century, particularly by Cassella.

Azoic dyes synthesised on the fibre were developed in Germany in 1889, and were able to give exceptionally brilliant red shades with good fastness on cotton.

Similar fastness was obtained with the vat dyes, although they are deficient in the red area. The first of these, Indanthrene Blue RS, appeared in 1901, and is related chemically in some ways to both alizarin and indigo. The BASF range available soon expanded to include yellows, violets, greens and browns.

This group of dyes generally had exceptional fastness properties, and is still seldom surpassed today in this regard.

The indigoid and vat dyes all required a reducing solution to apply them to cotton, and then had to be reoxidised to return to the colour required; that is, they were not 'direct' dyes. In spite of this relatively complicated process, their outstanding properties soon gave them an important role in dyeing.

The idea of manufacturing red azoic dyes in the cotton fibre was extended and made easier in 1911 by modifying the beta-naphthol in the both to solubilise it. It was not widely used until the 1920s because until that time yellows were not available.

The difficulties of controlling the vat dyeing process resulted in the first of the soluble vats in 1924. These could be applied to the fibre, and then oxidised to break off the solubilising group and fix the dye in the fibre.

1.7.8 Premetallised dyes

Wool dyeing received a boost in 1911 when Bohn, the discoverer of Indanthrene Blue RS, developed a way of incorporating chromium in dyes before application, rather than applying the chrome and the dye to the fibre in succession. Ciba produced the first range of 1:1 premetallised dyes in 1911.

Ciba followed this with copper complex dyes for cotton, which had excellent light fastness, known as the chlorantine light-fast range.

1.7.9 Cellulose acetate and disperse dyes

Apart from disrupting the manufacture of dyes in Europe, the First World War introduced new problems for the dyer. Cellulose acetate or 'artificial silk' had been developed, but there were no dyes that could dye it. The result of extended efforts by many chemists was to produce a finely dispersed, essentially insoluble, dye which would go onto the fibre from its dispersion. From this, disperse dyes were born. New fibres continued to appear. Nylon could be dyed with acid, premetallised and disperse dyes, polyester with disperse dyes and

acrylics with the basic dyes – the original types developed by Perkin and others – although new forms were also developed.

1.7.10 Reactive dyes

The most significant development since World War II has been the development of reactive dyes for cotton and viscose, which overcame many of the fastness limitations of direct and sulphur dyes and gave a brilliance never before possible across the colour gamut. The Procions were released by ICI in 1956, just a hundred years after Perkin's original discoveries. They gained their fastness by becoming chemically a part of the cellulose.

1.8   Synthetic dyes – advantages and impact

Thus, synthetic dyes are now the dominant product used. They give excellent properties in application and use, and are more consistent in those properties than natural materials. The methods of application are frequently simpler and give more consistent results than natural dyes. Shades between those of individual dyes are readily obtained as each range of synthetic dyes is more compatible and products can be mixed. This was not often possible with the natural dyes, as specialised methods were required for each product.

The history of dyes is essentially the history of chemistry. It has been mankind's desire for self-adornment that has resulted not only in new colours, but many of the products of chemistry that we accept as commonplace today.

2. Theory of dyeing

Before explaining any practical dyeing it is important to understand what causes dyes to be attracted to fibres and then to be retained by them. It will then be easier to understand why dyeing procedures have been developed in the way that they have.

2.1 Chemical bonding and dyeing

Dyestuffs are tincturially* very highly coloured molecules. Commercially produced dyes are mixed with large quantities of diluent. Common diluents are sodium sulphate and dextrose. The reason for diluting a dye is that the tinctorial strength of pure dye is such that only a few grams of pure dye would be required for all pale and most medium shades. This would lead to too great an inaccuracy in weighing in the colour store.

(*Tincturilly means 'of or for dyeing'.)

Dyeing occurs in water. In modern dyeing machines there is about 10 times more water than fibre; for 100 kilograms of fibre, typically you'll find 1000 litres of water. One kilogram of commercial dye on 100 kilogram of fibre gives a one per cent depth dyeing. For most cases this would be a medium type shade.

If you consider that only about 25% of the one kilogram of dye is pure dye, and this is dissolved in 1000 litres of water, this is a ratio of one to four thousand. The dye molecule therefore has a long way to travel to locate the fibre. Considerable forces must be at work then to achieve this.

In dyeing there are four different types of forces of attraction or bond at work: ionic bonds, covalent bonds, hydrogen bonding and Van Der Waal's forces.

2.1.1 Ionic bonds

These bonds occur when one atom donates an electron to another and so sets up an electrical attraction between the two. These are primary bonds and are strong. They are effective over large distances and are like the forces of magnetic attraction. They occur due to the loss or gain of electrons.

Dyes are coloured organic salts and in water a salt divides into two ionic fragments. One ion will be positively charged, the other negative.

Acid dyes split into a coloured negative fraction and an uncoloured positive fraction. Acid dyes will therefore bond with and give colour to fibres that have, or can be induced to have, a positive charge. Wool in acid conditions is such a fibre.

Basic dyes do the reverse and so will be attracted to any fibre that has a negative charge. For instance, wool at a pH greater than 4.5 has basic dye sites, the number of which increases as the alkalinity increases. Acrylic fibres that have been modified to provide basic dye sites also form bonds with basic dyes.

2.1.2 Covalent bonds

Covalent bonds are also primary bonds and are strong. They are formed by atoms sharing a pair of electrons. Ionic bonds occur because some elements, notably the metals, can donate an outermost electron to another atom, which sets up the electrical attraction between the two. Other elements find it less easy to donate electrons and so a sharing system is set up. However, the sharing is less than equal and so there is some electrical attraction also.

In all bonding, bonding will take place and be stable if, after the reaction, the product that is produced exists at a lower energy level than previously. In covalent and ionic bonding this

is achieved with the filling of the outer electron shells of each atom so it gains the nearest noble gas configuration. The noble gases neon, argon, krypton, xenon and radon, are chemically inert and therefore unreactive. A high degree of energy will be required then to break these bonds. The strength, type and degree of chemical bond between a dye and a fibre will control its fastness, in particular its wet and chemical fastness.

Reactive dyes for cotton and wool are the only dyes which use this bonding system as their primary method of attachment. As reactive dyes are primarily acid dyes which have had a reactive group attached, their increased wet-fastness over acid dyes can be solely attributed to the covalent bond.

2.1.3 Hydrogen bonding

Hydrogen bonding is a secondary bonding system and is about one tenth the strength of covalent bonds. It operates and is affective only over short distances in comparison to ionic bonds. Hydrogen bonding occurs where there is attraction between the negative part of one molecule and the positive part of another.

Hydrogen bonding comes about in covalent bonds because one of the atoms in the bond is more electro negative than the other. Oxygen and nitrogen are the most electro negative elements and they exert an uneven pull on the electrons of covalent bond atoms. The oxygen being slightly negative, the other atom in the molecule is slightly positive. This allows weak attraction between the negative portion of one molecule and the positive portion of another molecule.

In dyeing, the direct dyes for cotton utilise hydrogen bonding to form bonds with cellulose. The most successful direct dyes appear to be long, linear, multiple azo molecules which have hydroxyl groups spaced along their length at approximately the same spacing as the hydroxyl groups of cellulose.

The weakness of the hydrogen bond is shown by the generally poor wet fastness of direct dyes and the poor exhaustion shows it has only short range effect.

2.1.4 Van Der Waal's forces

Van Der Waal's forces of attraction, sometimes called mass attraction, is a very complex subject. In its simplest form, molecules may overlap and stick together. The larger the molecule and the more dispersed its electrons, the easier and greater the overlap. Dye molecules are generally large and flat like a sheet of paper so they can overlap the large polymeric fibre molecules to a high degree.

Like hydrogen bonds they are weak and can only come into effect over short distances. However, the ionic bonds control affinity; that is, the propensity of a dye to leave solution and travel into the fibre or, in dyers' terms, exhaustion of the dye bath, without the secondary forces of hydrogen bonding and Van Der Waal's forces to anchor the dyes firmly giving substantivity.

Substantivity is a quality colourants have if they are to be useful dyes. The higher a dye's substantivity the greater its wet fastness properties. It can be thought of as being like the stickiness of glue. It is increased by increasing molecular size and accounts for the wet fastness improvement of milling dyes over acid levelling types on wool.

The four bonding forces are listed below from strongest (covalent) to weakest (Van Der Waal's forces):

Bond type	Relative strength
Covalent	30
Ionic	7
Hydrogen	3
Van Der Waal's forces	1.

2.2   The kinetics and thermodynamics of dyeing

Kinetics is the study of the movements in atoms that occur when energy is applied. Thermodynamics is the movement or transfer of molecules across phases; for example ice, water and steam are the solid, liquid and gaseous phases of the H_2O molecule. Obviously, ice has very little kinetic energy, water has more and steam has a lot of kinetic energy.

As more energy is supplied to a system the molecules will start to vibrate. If energy is increasingly applied, bonds will break and the atoms will move randomly. Bonds may reform elsewhere or be constantly breaking and reforming. To a dyer this is called 'migration'.

There are five phases in the progress of a dye from the aqueous phase of the dye bath to the solid phase of the fibre.

Phase one is approach. The dyes are evenly dispersed or dissolved in the dye bath. Gradually they become more and more aware of where the fibre is located and begin moving towards it.

Phase two is adsorption onto the surface of the fibre. At the sub-microscopic level fibres are very irregular structures and dye becomes lodged on the surface, half in solution and half in the fibre. The adsorption phase is speeded by having more porous fibres, lower crystalinity fibres or undrawn fibres, which don't have a skin/core relationship where the skin is more crystalline then the core.

Phase three is penetration of the fibre surface by the dye molecule. The process of adsorption and penetration together is called 'absorption'.

Phase four is migration. The dye has to penetrate the amorphous structure of the polymer chains and is trying to locate a dye site. If the kinetic energy is low and the substantivity of the dye is high, bonding will occur at the first available dye site and unlevelness could result. More kinetic energy could be supplied to break the bond, but this is only possible if no fibre damage results. If fibre damage would result from increasing the available kinetic energy or if doing a pale dyeing, the dyer will control levelness by controlling the number of dye sites.

Phase five is fixation and is the end of the dyeing process. A stable bonding system of some sort is established and the dyeing is level. In the case of reactive dyes this is virtually irreversible.

2.3   The effect of temperature

The effect of temperature on dyeing is the same as on any chemical system. Increasing temperature increases the rate of reaction. This means the rate of dyeing or the strike rate of the dyes is increased. Too high a rate of temperature rise will result in unlevelness. If the

dyes have poor migration due to high substantivity or strong and irreversible bond formation, then unlevelness will result.

Some dye-fibre systems will require higher dyeing temperatures than others. Note that in the following table different classes of dye on the same fibres have different activation energies. This indicates that dye affinity is dependent on the polarity of the dye.

Activation energies for different dyeing systems		
Type of Dye	**Fibre**	**Activation energy**
		(kcal./mole)
Azoic coupling components	Viscose rayon	10
Vat	Viscose rayon	12.5
Direct	Viscose rayon	14
Equalising acid	Wool	21
Milling acid	Wool	29
Disperse	Polyester	40

Wool dyeing

An activation energy of 10 kcal/mole means dyeing can be done at room temperature 20 kcal/m is 60°C to 80°C, 30 kcal/m is 100°C and 40 kcal/m would require a dyeing temperature of 130° to 140°.

Note that wool only requires 60–80°C, but is commonly dyed at the boil. This is because substantivity reduces with higher temperature so migration can increase, giving levelness. Doing this also reduces exhaustion but as the rate of dyeing is increased a shorter dyeing time results. This improvement in productivity is worth the loss of yield from the dye.

2.4   The effect of pH

The pH is the measure of acidity or alkalinity. It is a measure of hydrogen ions in solution, measured on a scale of 0–14; below 7 is acid, above is alkaline.

The pH is important in controlling dyeing in two ways. Firstly, dyes themselves may be pH sensitive; in fact, one of the first direct dyes, Congo Red, is now only used as a pH indicator. Secondly, with certain fibres, notably the protein fibres, the pH will control the number of dye sites. In wool at pH 4.5 the number of dye sites is at a minimum and equally distributed between positive and negative. As the pH becomes more acid more positive dye sites are produced. Going to pH above 4.5 increases the number of negative sites.

Note that wool is dyeable with acid or basic dyes, depending on pH. Note also that the table only indicates acid levelling dyes and that these cannot fully exhaust.

2.5   The effect of circulation on dyeing

Good circulation is important to speed up the approach phase of a dyeing. This is because as the rate of dyestuff molecules circulating through the fibre per unit time increases, the chances for adsorption increase.

If circulation is slow or uneven, not thoroughly penetrating every area of the fibre, unlevelness could result. Slow circulation gives unlevelness because a dye molecule may exhaust from the dye bath and not be replenished. This will give a patchy dyeing with the appearance of light and dark dyed areas. Poor circulation due to machine liquor flow dead spots gives white patches where no dye-charged liquor is flowing. From the dyer's point of view the best type of circulation is high-volume, low-pressure circulation, like a wide, deep river. This gives the widest area of penetration with minimum fibre damage. Low-volume, high-pressure flow is undesirable in a dyeing machine.

Dyeing machines are characterised as having either liquor flowing and fabric still, the liquor still and the fabric moving or both fabric and liquor moving. Modern soft-flow dyeing machines offer complete dye bath circulation in one to three minutes. These machines also offer the fastest rates of temperature rise and shortest dyeing times in comparison with machines with lower volumes per unit time of circulation.

2.6   The effect of auxiliaries

The auxiliaries used in dyeing should be differentiated from the common inorganic chemicals like acids, alkalis and salts. Auxiliaries are more complex, mainly organic molecules. Their function is to improve dispersion, reduce inter-fibre friction, between fibres and between fibres and metals, level or retard dyeings, soften fibres and improve fastness and so on.

2.6.1   Auxiliaries used before or during dyeing

(1)   Anti-foams

Anti-foams have traditionally been based on silicone oil, which needs careful emulsification. They are very effective as knock-down anti-foams and reduce tangling in high circulation jets. Their disadvantage is in 'cracking out' of emulsion leaving faults that are very difficult to correct on the fabric. Later types based on surfactant solvent mixtures and called de-aeration agents are not as good-knock down agents. They work by collapsing micro disperse air emulsified into the dye liquor by highly turbulent dyeing machines or too many foaming auxiliaries. They have the added advantage of reducing the dye liquor's surface tension and improving penetration of yarns.

(2)   Scouring agents

Scouring agents are surface active agents with a high degree of detergency. They have the ability to remove dirt or other impurities from textiles and hold them in suspension.

Positively, negatively and unchanged versions are available depending on fabric type and following dyeing process. They should be properly removed before dyeing and be non-foaming. Some types are used in single-bath scour-dye methods. Their effectiveness is almost always related to the price.

(3)   Levelling agents and retarders

Levelling agents and retarders can work on the fibre, the dye or both at the same time. There are positive, negative and uncharged types. Those that work on the dye act to keep it in solution longer, only gradually releasing it to be absorbed by the fibre. The others block dye sites on the fibre, either temporarily or permanently. These act like colourless dyes. Specialist types are available to cover up fibre affinity differences.

(4)   Dispersing agents

Dispersing agents are mainly for disperse dyes and are usually negatively charged. Dispersing agents are used in disperse dyeing of polyester to prevent the dyestuff agglomerating and becoming insoluble and crystalising out onto the surface of the fibre.

(5)   Carriers

Carriers allow dyeing at lower temperatures by promoting swelling of the fibre. Their classic use was in allowing polyester to be dyed at the boil when pressurised machines were not available. As they are usually highly aromatic and somewhat objectionable in open dyeing machines their use is being restricted more and more. Special carriers have been developed for dyeing wool at 80℃. Brighter dyeings and less fibre damage are claimed.

(6)   Exhaustion synchroniser

Over recent years what might be called exhaustion synchronisers have been produced. With specially selected disperse dyes they achieve rapid dyeing cycles. They work by lengthening the temperature range over which the dyes exhaust. The strike rate is less, without a peak. The strike can start from **a** lower temperature. They offer reduced dyeing time by allowing faster rates of temperature raising and shorter time at top dyeing temperature, or a lower top dyeing temperature for normal dyeing time. Generally, they also improve dispersion and exhaustion and so aid repeatability of recipes.

(7)   Fibre protective agents

Fibre protective agents are used in two different areas. As lubricants they coat fabric fibres, preventing chaffing. In jet dyeing they allow higher fabric speeds, thus allowing more dyeing capacity or shorter dyeing times. In wool dyeing they form protective colloids around the wool to prevent fibre damage from high temperatures.

2.6.2   Auxiliaries used after dyeing

Various after-treating agents are commonly used in dyeing. They are mostly used to increase wet fastness but some improve light fastness. The more important are the syntans for acid dyes on nylon, while cotton is the most after-treated fibre. For cotton, many light or wet fastness improvers are available based on positively charged (cationic) auxiliaries; their main use naturally is for direct dyes. They also help reduce patchiness due to migration while the fabric is wet awaiting drying. Fixative resins for application to specially developed direct dyes give very good washing fastness and have revived interest in direct dyeing in recent years.

Softeners do exactly what their name implies, adding softness to synthetic fibres or replacing natural softness that the dyeing process has stripped off. They may also impart added absorbency and raising or brushing character to the fibre.

Softening is generally the last process before removal from the dyeing machine. Softeners, like other auxiliaries, sometimes impart undesirable qualities; for example, they can yellow fibres when drying is done and so reduce whiteness of white and can significantly change the shade of pale blues. In general, they reduce the wet fastness of dyeings where the dye or the thermal treatment it receives causes the dye to bleed into the softener over time. Softener, of course, is not as firmly anchored to the fibre as the dye was and so washes out, causing stains.

3.   Choice of dyes

3.1   Properties of dyes

The four properties dyes must have are intense colour, solubility, substantivity or reactivity, and fastness.

Intense colour

Dyes are organic molecules that are unsaturated and have certain substituent groups. The unsaturated part of the molecule is called the chromophore and it gives the dye its colour. Other groups called auxochromes are required to intensify the colour. This will be discussed in detail later in Dyeing Theory.

Solubility

Dyeing takes place from aqueous solution, so that the dye must contain groups giving solubility in water. This solubility may only be needed temporarily during dyeing, the dye later being treated on the fibre so it becomes insoluble, as is the case with vat dyes.

Substantivity or reactivity

Substantivity is the ability to be absorbed and retained by the fibre; reactivity is the ability to be chemically combined with it. The substantivity of a dye for a given fibre and application method is determined by the presence of one or more specific groups, the cross-sectional area of the dye molecule and its total volume. The reactive dyes are retained by the fibre because they form a covalent bond with the fibre molecules. A reaction takes place between a specific chemical substituent group in the dye molecule and part of the fibre molecule.

Fastness

The ability to withstand the treatment the fibre undergoes in the processes after dyeing and in normal use.

3.2   Choosing dyes

The correct choice of dye in any given application requires knowledge and practical experience, not only in deciding which class of dyes to use, but also making the decision as to which dyes within that class are the most appropriate. Colour is obviously an important consideration but the technical properties are no less important. One reason for the huge numbers of commercial dyes that are available is that any textile material will have to withstand a variety of processes during manufacture, and in use will be subjected to different types of wear and tear. Some examples of this are given below:

- During manufacturing, woollen fabrics, such as blankets and tweeds, undergo a vigorous mechanical treatment known as milling. Unless 'fast to milling' dyes are used, colours are likely to bleed.

- The stage in the processing sequence at which the goods are to be dyed affects the choice of dyes. When dyeing fabric only, the most level dyeing dyes are used because it is critical that there be no variation in the depth of colour through the goods. In dyeing loose fibre, levelness is not as great a problem as the fibres, and hence any variation in their colour, will be blended and mixed during subsequent processing into yarn.

- Many textiles in use have to be able to withstand very severe conditions, for example, exposure to sunlight or repeated washings, so fabrics for outerwear or curtains must have very high fastness to light, especially in Australia (compared with North America or Europe). Fabrics for awnings or outdoor furniture must also have very high light fastness, as well as be able to withstand rain and, perhaps, chlorine. Care should always be taken when a textile is going to be used for an end use for which it was not originally intended, for example, the use of fabric intended for ladies apparel for swimwear. The fabric should be tested for fastness to light, water, seawater and chlorine.

These are only some examples of the factors to be considered in choosing dyes. Others, related to your work experience, should occur to you.

3.3   Manufacturers' dye names

Dye manufacturers use a coded description to distinguish their products from those of other manufacturers and identify each individual dye in the product range they offer their customers. This code can be largely understood and used to give some information to the dyer. For example, if a manufacturer had a dye called Supranol Fast Blue 4R200, the following information could be deduced.

The brand name, in this case Supranol, would tell us which manufacturer produced this dye and indicates that this is an acid milling dye. Supranol Fast tells us that it is a particular class of acid milling dye. Blue describes the hue of the dye. Blue 4R indicates that this is a reddish blue dye, redder than Blue 2R for example. Thus, R, B, G, are used to represent the tone of the hue. These letters represent the German name for the colours, that is, R = rot (red), B = blau (blue), G = gelb (yellow). So a blue might be described as R (reddish) or G (yellowish) and a red as bluish or yellowish in various degrees. The suffix G applied to yellows denotes greenness. A suffix may also indicate some special quality, for example, LL for 'fast to light' or FF for 'very bright'. At times, the meaning of the suffix is known only by the manufacturer.

The last part of the code is a figure indicating the comparative strength of the dye. In this case the figure 200 indicates a dye of twice the strength of the standard strength of the dye, the standard strength being taken as 100 or 100% strength. Dyes are produced at a very strong strength which may have limitations in the actual dyeing process. A dye may be so strong that it will not dissolve readily in water and may have a tendency to dye unlevel. So the manufacturer will dilute the product with diluents such as salt, dextrin or dispersing agents and adjust it to have a predetermined dye strength. If it is diluted down to the standard strength, an 'S' could be added to the dye name to indicate this, for example, Supranol Fast Blue 4RS.

Most dyes have no suffix indicating strength and you con assume they are of standard strength. At times a dye may be available commercially in two strengths or the powder and liquid form of the one dye may be of different strengths.

3.4   Selection of dye classes for specific fibres

Principal dyes used for fibres

This section of the topic is a brief summary of the main classes of dye used for the fibres in common use.

3.4.1 Polyester

Disperse dyes

Disperse dyes are the principal class of dyes used on polyester. Disperse dyes vary considerably in their properties and are grouped into similar types by manufacturers. The principal property used to classify the dyes is the heat fastness or ease of sublimation of the dye. Manufacturers indicate their classification methods in pattern cards; for example, ICI uses an A, B, C, D classification, where A dyes have low heat fastness, but diffuse into fibres easily; whereas D dyes diffuse slowly but have excellent heat fastness. The A dyes have low energy requirements in dyeing, the D dyes high energy requirements, and B and C dyes have intermediate energy requirements.

Disperse dyes are able to produce a wide range of shades with good fastness on polyester. A range of methods is available for exhaustion and continuous dyeing.

3.4.2 Cellulosic fibres

Cotton and viscose can be dyed with the following types of dyes.

Reactive dyes

Reactive dyes can produce a very wide range of shades with good fastness properties. Continuous and exhaustion dyeing processes are available. The particular reactive systems used determine the dyeing conditions, temperature and times required. Their introduction has revolutionised the methods, colour range and properties of cellulose dyeings.

Direct dyes

Direct dyes can produce a reasonable range of shades with adequate fastness properties. provided they are after-treated with copper and/or cationic agents. They are generally applied by exhaustion methods, although some continuous methods are available. The shade range is limited in the green, red and violet areas, compared with reactive dyes. These are relatively cheap dyes.

Vat dyes

Vat dyes have very high fastness properties, but have a more limited range of shades than the direct dyes, particularly in the red and, to some extent, yellow areas. Methods are complicated compared with those above, both in exhaustion and continuous dyeing contexts, because the dyes must first be reduced then diffuse into the fibre before re-oxidation and soaping occur.

Solubilised vats are also available, which avoid some of these steps.

Vat dyes are categorised by manufacturers according to the severity of the reduction treatment necessary for optimum yields.

Both forms of vat dyes are expensive, but their fastness properties justify the expense.

Azoic (napthol) dyes

Azoic dyes are actually manufactured on the fibre and, provided after-soaping is adequate, give excellent wet fastness properties. The shade range is particularly strong in the red area, but is deficient in the blue and green areas. Light fastness is excellent in heavier depths.

The methods are relatively simple, but require careful control of conditions, particularly temperature, which must be near freezing point during the diazotisation and coupling part of the process.

Exhaust and continuous methods are available.

Sulphur dyes

Sulphur dyes are similar to vat dyes in that they are reduced, diffused into the fibre and then re-oxidised and soaped.

Light fastness is generally not high and the shade range is limited to dark, dull shades and does not include bright shades.

Soluble forms of sulphur dyes are also available.

Both forms can be applied by exhaustion and continuous methods.

The great advantage of the sulphur dyes is their economy, particularly in the case of the blacks.

3.4.3 Polyamide

In the case of polyamide, there are a limited number of dye sites available, which can affect the depth of shade possible and the process and auxiliaries used in the dyeing. As well, the distribution or access to dye sites may vary. The ability of the dyes to cover these variations is an important factor.

Acid dyes

Acid dyes are applied to the fibre under acid conditions. They have a very wide shade range and good fastness properties. Wet fastness can be improved by after-treating (backtanning) the dyeing in some cases.

Compatibility within combinations is important, as blocking effects and differential coverage of yarn irregularities may result if selection is not carefully done.

Premetallised dyes

Premetallised dyes are applied to polyamide under slightly alkaline conditions, and give full depth dyeings with excellent fastness properties. The shade range is reasonable, but not as wide as with acid-dyes, but the dyes are not as critical with respect to compatibility in combinations. Coverage of yarn irregularities is good.

Disperse dyes

Disperse dyes are applied in light to medium shades to polyamide. The wet fastness in heavier shades is not high, and light fastness in pale shades is also limited. However, as disperse dyes do not require specific sites, they will cover irregularities in the distribution of dye sites. Blacks are sometimes produced with disperse diazo blacks.

Reactive dyes

Special reactive dyes for polyamide, the Procinyls, have been developed, they have a moderate shade range although light and wet fastness properties are excellent. Coverage of irregularities is excellent.

Normal reactive dyes can be applied to polyamide under acid conditions, but are subject to the same limitations as acid dyes.

3.4.4 Polyacrylonitrile (acrylic)

Basic dyes

Basic dyes are used for medium to dark shades on acrylic fibres, and if carefully selected will give excellent light and wet fastness properties. Because rapid exhaustion occurs when

the glass transition temperature is passed, it is important that dye combinations are compatible, otherwise uneven blotchy dyeings will result.

Retarders are added to control the rate of dyeing. Manufacturers' pattern cards provide calculation procedures which will give the quantity of retarder to add. The range of shades possible is excellent in all colour areas, although there may be difficulties in building up sufficient depth in heavy shades because of the limited number of dye sites available.

Disperse dyes

Disperse dyes are applied to acrylic fibres near the boil. Only pale shades are obtainable but there is little difficulty in levelling the shades. Light fastness is good if dyes are carefully selected. Blacks can be obtained using disperse diazo dyes.

3.4.5 Wool

Reactive dyes

Reactive dyes are applied to wool to enable bright shades with good wet fastness to be obtained.

Reactive dyes have also been developed which are based on 1:2 pre-metallised dyes, which, while not as bright, do give excellent wet fastness.

Acid dyes

Acid dyes are so named because the classical methods of application require them to be applied in strongly acid baths. Now, dyes from the wide range of acid dyes available are grouped according to the acidity of the dye bath required to apply them.

- Level dyeing or equalising acid dyes are applied at the boil in strong acid and Glauber's salts. Under these conditions, they give level results, but have only moderate wet fastness properties.

- Milling dyes are applied under weakly acid or neutral conditions, and do have good wet fastness properties. Their name comes from their ability to withstand 'milling', that is, treatment in a warm, alkaline soap solution under roller pressure for a considerable time. Milling is a treatment used to close up woven structures by felting the wool. Levelness may be harder to obtain on piece goods than with the equalising acid dyes.

Chrome dyes

Chrome dyes are very similar to acid dyes, but cannot be used in the same way because of low wet fastness properties. However if the dye is treated with a chrome mordant, it will become insoluble and fixed in the fibre. Fastness is excellent to light and washing, but the shade range is not bright, and is mainly in the tertiary area, that is, browns and greys.

Care must be taken to ensure that the chrome complex is formed in the fibre as insoluble particles on the surface can give low rubbing fastness.

Premetallised dyes:

Rather than follow through the relatively complex mordanting process, manufacturers have incorporated chromium into dye complexes, which can be applied as acid dyes.

Two distinct groups exist:

- 1:1 – premetallised dyes. which are applied from strongly acid solutions. The dyes are level dyeing, have excellent light and wet fastness properties and will withstand light milling treatments

- 1:2 – premetallised dyes, which are applied in weakly acid conditions, and give excellent wet and light fastness. They also cover damaged wool very well.

3.4.6 Secondary cellulose acetates

Low sublimation fastness disperse dyes are usually the preferred dyes for secondary acetate, for example, the A and B class dyes in the ICI classification. These groups have the ability to build up quickly to reasonable depths.

Dyes must be selected from these groups so that they are compatible, as secondary acetate is a delicate fibre, and frequently dyed on jigs, which may emphasise differences.

Care is also necessary to ensure that gas fume fading of anthraquinone blues on secondary acetate is prevented by incorporation of a gas fading inhibitor in the treatment. The range of shades on secondary acetate is reasonably wide, and good light fastness can be obtained in most depths. Wet fastness however is not as good, particularly in heavy depths.

3.4.7 Cellulose triacetate

Dye selection for cellulose triacetate is similar to that for polyester. Dyeing is done at or near the boil, with little danger of saponification occurring. The range of shades possible is as wide as on secondary acetate, but the light fastness tends to be a little lower, and the wet fastness is generally good in comparison with that on secondary acetate. Gas fume fading is also a factor on triacetate and must be prevented by the use of gas fading inhibitors.

4.   Dyestuff classes suitable for wool

4.1   Acid dyes

Acid dyes are a simply applied group of dyes able to be applied to wool and polyamide in a wide range of shades with good fastness properties.

The application conditions are similar in principle for both fibres. The response of individual dyes to them results in classification methods for each. The Society of Dyers and Colourists' classifications are followed in these notes, and are similar to most other classifications.

As the molecular weight of the dye molecule increases, acid dyes require a less strongly acid dye bath to obtain adequate exhaustion.

Classification for wool

On wool, they are accordingly classified into four groups:

Acid		pH	Description
Group 1	Sulphuric acid	2.5–3.0	Equalising or levelling
Group 2	Formic acid	4.0	Equalising or levelling
Group 3	Acetic acid	4.5–5.0	Milling
Group 4	Ammonium sulphate	6.0–8.5	Neutral dyeing

With Groups 1 to 3, 10–20% of Glauber's salt is also added. The classification is not rigid, and some dyes can cross classification boundaries for alternative application methods.

Group 1

The level dyeing or equalising acid dyes are rapidly absorbed at low pH. Dyes are generally applied from a dye bath containing 3–5% sulphuric acid and Glauber's salt. The dyeing should begin at or below 60℃, then be raised to the boil and held for 45 minutes. Levelling is improved by the addition of larger amounts of sulphuric acid.

Group 2

This group represents a compromise and contains two types of dyes:

- dyes applicable in sulphuric acid, but with improved levelness in formic acid with adequate exhaustion

- dyes applicable in acetic acid, but whose exhaustion improves with formic acid without affecting levelling properties significantly.

The application is as for Group 1, except for the acid used.

Group 3

Dyes in this group are generally of larger molecular size, have better wet fastness than Groups 1 and 2, but do not generally migrate as well. These dyes are known as 'milling acid dyes' as they have reasonable fastness to subsequent milling processes.

Dyeing begins at or below 50℃ with acetic acid and Glauber's salt. After being raised to the boil, it is held there for 20–30 minutes. If the bath is not exhausted at that point, further acid can be added.

Group 4

Dyes in this group require little acid and are known by the confusing name of 'neutral dyeing acid colours'. They have extremely high fastness to milling, but must be carefully applied to avoid unevenness.

Dyeing is begun at 60℃ or below in a dye bath with 2–5% ammonium acetate or ammonium sulphate. The bath is raised to the boil and held there for 45 minutes. The rate of rise should be controlled carefully if the dye is difficult to level. The dye continues to exhaust at the boil and the bath gradually becomes more acid as the ammonium salt begins to decompose and release ammonia to the atmosphere, that is:

$$NH_4 O.OCCH_3 \quad\quad NH_3 \quad + \quad CH_3COOH$$

ammonium acetate   ammonia   acetic acid.
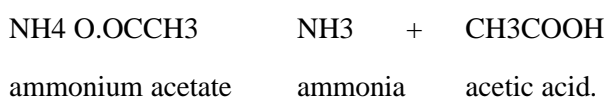
The acetic acid gradually acidifies the bath. In some cases, where exhaustion is still slow, additional acetic acid may be added to exhaust the last of the dye bath. The ammonium salt also assists in neutralising residual alkali from scouring of the wool, which could cause damage if excessive at dyeing temperatures. Thus, when large amounts of dye are being exhausted, the rate is limited by the neutral pH,and unlevelness is minimised, but as the rate slows, the pH drops and improves the degree of exhaustion.

Classification for polyamides

The classification of acid dyes for polyamide is analogous to that for wool, although only three groups are used:

- **Group I** – dyes with little affinity under neutral or weakly acidic conditions, but which exhaust under strongly acid conditions

- **Group II** – most acid dyes belong to this group, which exhausts onto polyamide in between pH 3.0 to 5.0

- **Group III** – dyes which exhibit a high affinity for polyamide under neutral or weakly acid conditions, that is, between pH 5.0 to 7.0.

The groups have a general relationship to those for acid dyes on wool but, as a particular dye may behave differently on each fibre, the relationship should not be assumed rigidly. A given acid dye will have a lower rate of exhaustion and better wet fastness on Nylon 6.6 than on Nylon 6 because of the higher proportion of crystalline matter in Nylon 6.6. Nylon 6 will permit the dye to build up faster and have better levelling properties.

Dyeing is generally done at the boil, with auxiliaries added to control levelling, rate of exhaustion and pH.

4.1.1 Particular considerations for acid dye on wool

Time of dyeing

Prolonged periods at the boil when dye additions are made can cause damage to the wool fibre. A reasonable time is necessary to allow the dye to be distributed evenly and penetrate the fibre adequately.

Levelness

It is desirable for fabric to be level after dyeing, although this is less critical for loose wool, stubbing, and to some extent yarns, as subsequent processing tends to minimise differences. Pale shades are more difficult to get level than dark shades. Equalising acid dyes have good levelling properties, and a higher degree of initial unlevelness can be tolerated as it will be eliminated during dyeing. Milling and neutral dyeing acid dyes must be applied level in the

first place as they have successively reduced abilities to subsequently level out. In these cases, careful control of the rate of rise of temperature is necessary. Unlevelness also occurs with these dyes when large additions are made, as the lowest pH and maximum temperature conditions are encountered, causing rapid strike. It may be necessary to compromise fastness properties and use equalising acid dyes for large additions.

Levelling agents can be added to assist. These are usually non ionic-cationic mixtures which restrain the dye from exhausting too rapidly. They may reduce the equilibrium exhaustion somewhat. The same agents usually are helpful in covering tippy and other damaged wools, whose rate of acceptance of dye varies.

Compatibility of dyes

Equalising acid dyes generally cause no difficulties in obtaining homogenous shades. However, milling and neutral dyeing acid dyes con sometimes result in dye selectiveness. The dyes chosen should be as alike in fastness properties as possible, as well as in application properties, rate of exhaustion, levelling and so on.

4.1.2 Particular considerations for acid dyes on polyamide

Dye affinity variations in the fibre

Chemical variations resulting in changes in the density of anionic end groups (that is, dye sites) present the dyer with a difficult problem.

Pretreating the fibre with an anionic blocking agent can assist, and dyeing at elevated temperatures up to 120℃ can be useful. The faults are less obvious in shades where differences are difficult to perceive, for example, whites, blacks, reds, yellow. The pretreatment assists because the fibre is in effect 'dyed' with a colourless agent, which then moves off, providing dye sites more evenly for the dye molecules to exhaust onto.

Levelling agents

As with wool, levelling can be important, particularly in pale shades. The anionic blocking agents used in pretreatment can assist in obtaining levelness, but cationic agents which complex the dye can also be used to restrain the exhaustion. Agents that increase the solubility of the dye in the dye bath will also improve levelness.

The presence of these agents in the dye bath can also ease the difficulties of making additions without reducing the temperature from the boil.

After-treatment to improve wet fastness

As noted above, good wet fastness on polyamide can be obtained, but the dyes used are prone to show affinity variations. If the choice of dyes is limited by the nylon source, dyes with lower wet fastness properties may have to be used. The wet fastness can be improved by the use of 'tanning' agents. Tannic and formic acids are applied together at 85℃–90℃ for Nylon 6.6 and 60℃–70℃ for Nylon 6. This is followed by tartaremetic treatment (potassium antimony tartrate), which interacts with the tannic acid and the fibre to form a surface skin which resists domestic washing treatments. This treatment tends to dull the shades and is expensive, both in chemicals and time consumed.

A simpler, cheaper treatment uses synthetic tanning agents which are generally anionic. Good fastness with most equalising acid dyes can be obtained in quite deep shades. Light fastness may be a little lower, and stiffen the fabric a little. The shade shift is not as great as with full back tanning treatments.

Saturation

Dye sites are limited on polyamide. Shade can be controlled only until saturation occurs. After that, the dye with the highest affinity will tend to occupy the sites.

4.2   Chrome dyes on wool

Chrome dyes are closely related to acid dyes, but the dyes have additional groups within them which enable them to form co-ordination compounds with chromium within the fibre. This has a number of effects:

- shade changes due to absorption of longer wavelength of light

- light fastness and wet fastness improves.

The complex forming process is a mordanting process. The dyes are applied in a similar manner to acid dyes, because they are of low molecular weight and not fast to alkaline and other wet treatments.

The chrome dyes are not as bright as acid dyes, and as they form 1:2 metal complex dyes in the fibre, have a similar range of shades to the 1:2 premetallised dyes. Generally, 1:2 premetallised dyes are used for pale to medium shades, and the chrome dyes for full shades.

Alizarine is a mordant dye and as the active component in madder was a widely used natural chrome dye. Logwood is the only natural mordant dye still widely in use. When only a few natural products were available the range of shades was extended by the use of different mordants. Aluminium gave the brightest shades, iron the dullest shades, copper and chromium the best light fastness and chromium the best wet fastness. These days, the variety of metals used in mordantry is unnecessary because of the wider range of synthetic dyes available. However, the ability to form complexes with many metals and to give resultant variations in shade and fastness means the bath must be free of any metals not required or results will not be consistent.

Method of applying chrome dyes

It is important not only to get the dye into the fibre evenly but also to get the 'chrome' in evenly and combined with the dye.

The 'chrome' used is generally potassium or sodium dichromate. Chromates are sometimes used.

Three methods are available:

- the chrome mordant method, where chrome is applied to the fibre before the dye

- the afterchrome method where the chrome is applied after the dye

- the metachrome method where dye and chrome are applied together.

The chrome mordant method

The chrome is applied under slightly acidic conditions at the boil. A small amount of acetic acid is added to the bath to neutralise any residual alkali from scouring which is released from the fibre at the boil. It is necessary for the chromium to be converted from the Cr (VI) to the Cr (III) state in which it will complex with the dyes. This change is accompanied by a colour change from yellow to greenish grey. To ensure that this change is complete, mild chelating agents may be added at the conclusion of chroming to remove Cr (Ill). This is also an advantage if the chrome dye is sensitive to oxidation. The use of the chelating agents e.g. potassium hydrogen tartrate gives a 'reduced chrome' mordant. Otherwise the mordant is known as a 'sweet chrome' mordant.

Chroming begins at or below 60℃ and, after being brought to the boil at approximately 1℃/minute, is held there for one to one and a half hours.

After the mordanting is complete, the fabric is well rinsed, and entered into a dye bath wet with acetic acid at 50℃, raised to the boil at 1℃/minute and held there for one to one and a half hours.

Additional acetic acid may be added to exhaust the dye. Fastness to milling can be further improved by after-chroming for 30 minutes after exhaustion is complete.

The method is the oldest, but takes longest as it involves a two-bath method. Some chrome dyes can only be applied by this method, but are not significant. Matching is relatively easy. The method is useful for pale to medium shades on worsted fabrics.

The after-chrome method

After exhausting the dye bath, the chrome is applied from the exhausted dye bath. Dichromate and dye must not be present simultaneously otherwise a chromium salt or chrome-dye complex may precipitate in the liquor or on the surface of the fibre. This will result in lowering of fastness properties. Dyeing is begun at or below 50℃ with a bath set with acetic acid and Glauber's salt, raised to the boil at 1℃/minute and held for 30 minutes. Further acid is added if the bath is not exhausted. After exhaustion, the bath is cooled back to 70℃, and the chrome added. The bath is brought back to the boil and held there for a further half to one hour, that is, until all the dichromate is reduced on the fibre.

With some dyes, a low pH will result in 1:1 as well as 1:2 complexes being formed. On subsequent alkaline milling, the shade will change due to conversion of the 1:1 complex to the 1:2 complex.

Matching of shade is more difficult because of the shade shift which occurs on chroming. However, the method gives the best fastness to milling in dark. shades as there is little chance of complexes being 'misplaced' on the fibre surface.

The metachrome method

With some chrome dyes it is possible to combine dyeing and mordanting in the same bath provided that:

- the dye can be exhausted from a weakly acid or alkaline solution, that is, pH 6.0–8.5

- the dye is not precipitated from solution by the chromium salt present

- the dye must not reduce the chromium salts in the bath.

A metachrome mordant is used, that is, one part of sodium chromate and two parts of ammonium sulphate. Because chromic acid is produced which reacts with the wool, alkali is produced, which reacts with the ammonium sulphate, releasing ammonia and maintaining the pH between limits. In fully enclosed vessels, release of the ammonia is not possible, resulting in an increasingly alkaline dye bath.

The dye bath is set with dye and the temperature is raised to 50℃. The metachrome mordant is added in a well diluted form. The temperature is raised to the boil at 1℃/minute and held for one hour.

Variations to chemicals and conditions may be recommended by different manufacturers, and to cater for the sensitivity of some dyes, but the basic approach is the same in all cases. The advantage of the method is its simplicity. It can be used for all shades except blacks. The pH conditions required are in a range in which iron and copper are insoluble, and hence dulling of shades is not likely.

However, in heavier shades, rubbing fastness may be low due to the formation of dye precipitates, and exhaustion may be incomplete due to the relatively high pH of the dye bath. The hue range is also limited compared with the chrome dyeing methods.

The method is not as widely used since the introduction of neutral dyeing 1:2 premetallised dyes.

4.3 Premetallised dyes

The chrome dyeing processes are relatively complex but give excellent fastness properties if correctly applied. The premetallised dyes give the same or nearly as good properties with respect to fastness. Provided they can be applied evenly, the application methods are simple, being essentially those for acid dyes.

Two types of premetallised dye exist:

- **1:1 premetallised dyes** – applied to wool from a strongly acid dye bath. These require a considerable amount of sulphuric acid in the bath in order to cover tippy and damaged fibres and obtain full wet fastnesses. Boiling is necessary to ensure full development of the shade as the chromium complexes with the fibre. These dyes have a slightly brighter shade range than chrome dyes, but their good all round fastnesses are counteracted to some degree by increased abrasion due to extended boiling under strongly acid conditions. The slow rate of exhaustion means that levelness is usually good and variations in the wool due to weathering or processing damage are well covered. Pieces which have been carbonised can also be dyed without an intermediate washing off and neutralising which would be required for dyes which required less acid conditions

- **1:2 neutral dyeing premetallised dyes** – a relatively recent development (1951), which are 1:2 chromium or cobalt complexes of azo dyes. These are applied to wool from a neutral or slightly acid dye bath (pH 5.5–7.0).

Because the sulphonic acid groups have been modified by the addition of methyl or amino groups, they do not ionise, but depend on hydrogen bonding for their solubility. It also means that their tendency to cause unlevelness, skitteriness or have lower wet fastness is minimised. The shade range is dull and similar to the 1:1 premetallised dyes, but includes more browns. The fastness is equivalent to that of the chrome dyes, except to resistance to the most severe wet treatments. As with the 1:1 premetalised dyes, dyeing is very slow.

The fabric or yarn is treated with ammonium sulphate or ammonium acetate at 40°C for 10 minutes, the dye added and the temperatures is raised to the boil at 1–2°C/minute. After half to one hour at the boil, the bath should be exhausted. Some manufacturers provide a small group of brighter milling acid dye with excellent fastness properties to be used as shading colours.

Premetallised dye on polyamide

As on wool, these are restricted to relatively dull shades, and have excellent fastness properties, particularly to light in pale shades. Their coverage of physical and chemical differences is not good, and as usual when wet fastness properties are good, levelling and migration properties are poor, that is, when the dye is on, it tends to stay put.

1:1 Premetallised dyes

Dyeing conditions are similar to those for wool, but the strongly acid conditions required for 1:1 premetallised dyes con result in fibre damage if prolonged. Selected dyes are able to be applied at a less acid (higher) pH, that is, 4.0 to 6.0, if depth and washing fastness on polyamide are critical. Self-colours, rather than trichromatic combinations, should be used.

The dye bath is set with:

- g/l weakly cationic auxiliary

- 3% ammonium acetate

- .05% acetic acid 30%

The liquor is brought to the boil at 1℃/minute and held for 45 minutes before sampling.

1:2 Premetallised dyes

Premetallised dyes have become important in the dyeing of nylon because of their excellent build-up properties. Considering the limited dye sites available, they are free from blocking effects and have very good light and wet fastness properties.

Selection of dyes from those available must be done with variable substrates, as the ability to cover affinity variations differs considerably. Those without solubilising groups tend to act as disperse dyes, and hence cover well. Trichromatic combinations are available with good compatibility. Back tanning can be used to further improve wet fastness properties, particularly in heavy shades.

The pH range recommended by manufacturers varies, but a typical dye bath would be:

- 3.0% ammonium acetate

- 2.0% blocking auxiliary (anionic)

- 3.0% complexing auxiliary (weakly cationic).

The fabric is entered and after circulation at 400℃, the dye is added. Temperature is raised at 1℃/minute, and dyeing may be done above the boil (up to 120℃) if suitable equipment is available. A small amount of anti-oxidant (for example, thiourea) may have to be added in high temperature processing to prevent the oxidation of anionic end groups, which will increase the sensitivity to photodegradation.

4.4   Reactive dyes on wool and polyamide

The conventional point of view is that reactive dyes were introduced in 1956 for cellulosic fibres. However, reactive dyes were in use on wool before this but it was not realised that the excellent wet fastness of some dyes was due to reaction with the wool until later.

The reactive dyes are essentially the acid and 1:1 and 1:2 premetallised dyes with a group added to permit covalent bonding to be established with wool. In some cases reactive dyes used on cellulose are also quite suitable on wool. The shade range possible is wider than with the conventional wool dyes. Brilliance tends to be associated with smaller dye molecules which also tend to have lower wet fastness properties. If they can be covalently bonded to the fibre, the brilliance is gained with high wet fastness.

For the same reason, the dyes can be highly sulphonated to enhance solubility as they are de-solubilised by bonding. However, this can result in tippy or skittery dyeing on damaged wool. Auxiliary products have been developed which have affinity for the wool and the dye to minimise the differential dyeing effects.

The appropriate pH for application varies from one type of reactive dye to another, depending on the reactivity of the group attached. Generally, the pH required is around 5. At lower pH, dyeing may be uneven and fixation poor, whereas at higher pH exhaustion may be poor.

While adequate exhaustion is important, fixation is also very important. The rate of reaction increases with increasing pH and if it is too rapid, unlevel dyeing may result as fixed dye cannot migrate. Reaction rates at pH 5 at the boil are usually adequate, but in full depths may be incomplete after an hour.

A final weakly alkaline treatment will ensure that fixation is completed, and full wet fastness gained. Most reactive groups also hydrolyse, and this hydrolysed dye must be removed or minimised. With most reactive groups, the minimum hydrolysis does occur at about pH 5, which assists in improving yields and fastness. Frequently, in the case of wool, the very small amounts of hydrolysis which result from the dyeing conditions used has sufficient affinity for wool not to affect the fastness appreciably.

This is particularly so with the Procilan (ICI) dyes which are 1:2 premetallised dyes. Any hydrolysed dye has the high affinity of the conventional premetallised dye. Cold pad batch processes with highly reactive dyes are possible. The wool is padded with dye, 300 g/l urea, wetting agents, acetic acid, thickening agent, and an antifoaming agent. The padded wool is batched for 24 to 48 hours then washed off in dilute ammonia at 60°C. Highly reactive dyes cannot be used by exhaustion methods because of skitteriness.

4.5   Summary of suitable dye classes for wool

Following are some examples of some dyestuff ranges marketed by Clariant, which are suitable for dyeing wool showing the pH at which they should be applied.

Clariant

1 Sandolan E dyes

Sandolan E dyes exhibit high migration power and produce good penetration.

Sandolan E dyes have provided particularly good results in piece dyeing and the hat industry.

In the furnishings and carpet sector the high lightfastness of certain dyes is of decisive importance.

Standard dyeing process
x% *Sandolan* E dye
1% *Lyogen®* MF Liquid
10% Glauber salt calc.
        pH 3 with formic or sulphuric acid.

Dye for 60 min at the boil.

Ternary combination
Sandolan Yellow E-2RL SGR
Sandolan Red E-BNL SGR
Sandolan Blue E-BGL 200 SGR
or
Sandolan Yellow E-2RL SGR
Sandolan Rubinole E-3GPL 150
Sandolan Blue E-FGL 250

This well balanced ternary combination covers a wide range of shades and produces on-tone dyeings on Wo/PA blends.

2 Sandolan P and
Sandolan Fast P dyes

Sandolan P and *Sandolan* Fast P dyes, which in the meantime have become a classic dye range, are dyed in the weakly acid region at pH 4–4.5 with acetic acid.
The dyes are readily combinable with each other.
Their main application is for hank yarn dyeing

Standard dyeing process
x%   *Sandolan* P or *Sandolan* Fast P dye
1%   *Lyogen* MF Liquid
10% Glauber salt calc.
1 g/l sodium acetate cryst.
        pH 4–4.5 with acetic acid.

Dye for 60 min at the boil.

opti/*an*   **Clariant**

3 Sandolan MF dyes

Sandolan MF dyes are the fastest acid dyes with good migration for yarn and piece dyeing.

Standard dyeing process
x%   *Sandolan* MF dye
1%   *Lyogen* MF Liquid
5%   Glauber salt calc.
1 g/l sodium acetate cryst.
        pH 4.5–5 with acetic acid

Dye for 30 – 60 min at the boil.

Standard ternary combination
Sandolan Golden Yellow MF-RL
Sandolan Red MF-2BL SGR
Sandolan Blue MF-GL SGR

On-tone dyeing for polyamide/wool blends
Sandolan Golden Yellow MF-RL
Sandolan Red MF-GRLN
Sandolan Blue MF-GL SGR

The *Sandolan* MF dyes are also suitable for dyeing silk and polyamide fibres as well as blends of these substrates with other fibres.

4 Sandolan N and Sandolan Milling N dyes

The *Sandolan* N and *Sandolan* Milling N dyes exhibit similar dyeing behaviour to the 1:2 metal complex dyes. They can therefore be applied as straight colours or as shading components with the *Lanasyn* dyes. The *Sandolan* N/*Sandolan* Milling N dye range contains highly wet- and lightfast products. If necessary, the dyes can be combined with the *Lanasan* dyes and are applied by the same dyeing process.

Standard dyeing process

x%   *Sandolan* N/*Sandolan* Milling N dye
1%   *Lyogen* MF Liquid
1 g/l sodium acetate cryst.
        pH 5 – 5.5 with acetic acid.

Dye for 30 – 60 min at the boil.

The *Sandolan* N/*Sandolan* Milling N dyes are also suitable for dyeing silk, polyamide fibres and a wide variety of blends.

optilan   **Clariant**

5 Lanasan dyes

Lanasan dyes are specially developed dyes for the fast, reliable dyeing of wool.

They exhibit optimum combinability and cover affinity differences between both the wool root and tip as well as wool qualities of different origins.

Standard dyeing process

x%   *Lanasan* dye
1%   *Lyogen* PAM Liquid
1 g/l sodium acetate cryst.
        pH 5 with acetic acid

Dye for 30 – 60 min at the boil.

Detailed information and further dyeing processes, illustrations and fastness properties are described in Shade Card No. 1547.00.88 "*Lanasan* CF dyes for wool, alone and in blends".

The *Lanasan* dyes are also suitable for dyeing silk and polyamide fibres as well as blends of these substrates with other fibres.

6 + 7 Lanasyn and Lanasyn S dyes

These well established dyes are distinguished by:

- high light and wet fastness standard
- reliable and simple dyeing process
- wide scope of application even on silk and polyamide fibres
- combinable with *Lanasan* dyes.

They are also suitable in many special areas such as for textiles in the automotive sector.

Standard dyeing process
x%   *Lanasyn, Lanasyn* S dye
1%   *Lyogen* PAM Liquid
1 g/l sodium acetate cryst.
       pH 5 – 5.5 with acetic acid.

Dye for 30 – 60 min at the boil.

The *Lanasyn* and *Lanasyn* S dyes are particularly suitable for the low temperature dyeing of loose stock or tops with *Lanasan* LT Liquid at 85°C. A good yield is obtained with no loss in the good fastness properties and maximum gentleness to the wool.

Other important application areas are silk, polyamide fibres and blends such as Wo/PES, Wo/PA, Wo/CEL.

opti*lan*   **✎Clariant**

8 Drimalan F dyes

The fibre-reactive *Drimalan* F dyes are distinguished by outstanding wet-fastness properties on wool, chlorinated wool and chlorine/Hercosett⁺ treated wool. These dyes are applied particularly to machine washable wool.

Standard dyeing process
Dyeing is carried out by the standard process or the rapid process with pH shift.
x%   *Drimalan* F dye
1–1.5% *Lyogen* FN Liquid
0–10% Glauber salt calc.
       pH 4 – 7 with acetic acid.

Dye for 30 – 60 min at the boil.

Aftertreatment (for dark shades)
Treat with ammonia at pH 8.5 for 20 min at 80 – 90°C.

These processes are described in detail in Special Shade Card No. 0306.00.85 "Dyeing machine washable wool".

5.   Application procedures for different dye classes on wool

For each of the dyestuff classes suitable for application to wool there are a number of dyestuff manufacturers who offer products that have equal technical merit. As they are too numerous to mention here, certain brand names will be used as examples only. However, prospective users should make their selections based on commercial considerations in their environment.

5.1   Dyeing wool with 1:2 premetallised dyes

There are many ranges of 1:2 premetallised dyes offered by numerous manufacturers. The example selected here is the LANASET range of CIBA.

Ciba LANASET dyes

Dyeing system for wool and wool blends.

Main characteristics of the LANASET dyeing system

Properties	Customer benefits
Broad shade range	Brilliant and restrained combination shades at all depths
	Brilliant shades with high wet and light fastness
Compact range with similar dyeing behaviour	Reduced inventory costs
	Excellent compatibility
	Easy dye selection
High fastness properties	High fastness to processing
	Suitable for all end products
	Suitable for carpets and upholstery
	Suitable for Oeko-Tex Standard 100
Dyeing pH 4.5	Minimum damage to the fibre
	Quality of the wool retained
	Higher spinning yields
Same dyeing method for all shade depths	Simple procedure
	More dependable results in production
High exhaustion	Good laboratory to bulk transfer
	Excellent reproducibility
	Minimal effluent pollution
Suitable for many blends	Flexibility for meeting changing market needs
	Only one dye range for the wool portion of different blends

General

The LANASET dyeing system is a versatile and comprehensive system for dyeing and printing wool, polyamide and silk. This pattern card provides recommendations for dyeing wool and wool blends. For application of LANASET dyes on polyamide and silk please refer to the corresponding publications.

The LANASET range comprises modified, tinctorially strong 1:2 metal complex, acid and reactive dyes with high wet and light fastness. The dyes cover the shade spectrum systematically. Almost all fashion shades can be produced economically using simple combinations of these dyes. Nearly identical dyeing properties and high exhaustion result in excellent compatibility and reproducibility.

For all depths of shade LANASET dyes are applied at pH 4.5 – the isoelectric region of wool – leaving the fibre in excellent physical condition. The auxiliary ALBECAL SET, designed especially for the dye range, ensures safe and level dyeing. LANASET dyes are suitable for dyeing wool in all its forms, especially loose stock, stubbing and yarn. In addition, the LANASET range is highly suitable for blends of wool with numerous other fibres, including polyester, polyamide, silk, acrylics and cellulose.

The pattern card contains useful information on pretreatment, bleaching, fluorescent whitening, dye selection, dyeing procedures including blend dyeing, and textile auxiliaries. Dyeing parameters are also detailed.

All dyes are illustrated as self-shades at several depths and in combination dyeings. Fastness data and details of application properties complete the pattern section.

Outlets

The LANASET range is suitable for dyeing wool as loose stock, stubbing, yarn and piece for the following outlets:

- women's and men's outerwear, uniforms

- knitgoods, hand and machine knitting yarns

- household textiles, blankets and upholstery

- floor coverings

- textiles made from fine animal fibres, for example, cashmere, mohair.

Dyeing

Dissolving the dyes

Paste the dye cold with soft water.

Add hot water (60–90℃/140–194℉) and boil up briefly with live steam if necessary.

Stir thoroughly (with high-speed stirrer if necessary).

Auxiliaries and chemicals should not be added during dissolving. For further details on solubility of the individual dyes, see the fastness tables in the pattern section. The temperature of dye solutions containing LANASET Red 2B should not exceed 60℃/140℉.

Dyeing chemicals

Penetration accelerants

CIBAFLOW CIR or ALBEGAL FFA is added to the dye bath to de-aerate and rapidly wet out the goods. These products also have a foam-suppressing effect.

Levelling agent

ALBEGAL SET is amphoteric and has affinity for both dye and fibre. For all shade depths, 1% ALBEGAL SET is used at liquor ratios from 8:1 to 25:1. Below 8:1 the amount should be reduced to 0.5%, above 25:1 it should be increased. ALBEGAL SET improves the compatibility of the LANASET dyes, promotes their migration and exhaustion, and greatly helps to ensure fibre and surface levelness. These effects can be improved still further by an addition of 5–10% Glauber's salt (particular recommended for dyeing yarn and piece goods).

Wool care product

MIRALAN Q improves the quality of the wool at all stages of processing. It reduces felting and setting during dyeing and has a lubricating effect. Carding and spinning properties of loose material are improved. In package dyeing, flattening on crossover points is reduced and bulk increased. In piece dyeing, running marks and felting are prevented.

Dyeing accelerant

MIRALAN TOP is a special dyeing accelerant for the LANASET TOP process to accelerate diffusion of LANASET dyes inside the wool fibre and shorten the dyeing time. The LANASET TOP process is recommended only for dyeing loose wool and tops.

Dye bath pH

Irrespective of shade depth and stage of processing LANASET dyes are applied at pH 4.5, the ideal pH for wool as it minimises fibre damage during dyeing. The pH is best set with a buffer of sodium acetate and acetic acid or with CIBATEX AB–45, a pH controlling agent, which sets the pH at 4.5.

Procedure for loose stock and slubbing

Conventional LANASET dyeing process
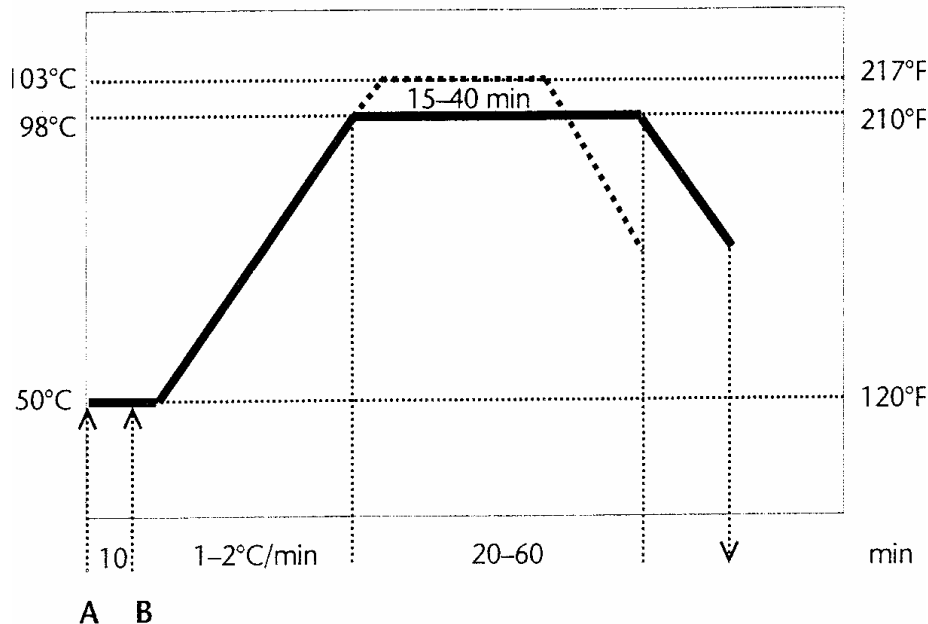
A	0.5 g/l	CIBAFLOW CIR or ALBEGAL FFA
	1 g/l	MIRALAN Q
	1%	ALBEGAL SET
	x%	formic acid 85%
	pH	4.0–4.5
B	y%	LANASET dyes

LANASET Top dyeing process

The LANASET TOP process for loose wool and tops shortens the dyeing process by means of the dyeing accelerant Ciba MIRALAN TOP. The benefits of the process are as follows:

- reduces dyeing time at the boil to half, improving productivity

- improves exhaustion to almost 100%

- reduced effluent load

- shorter rinsing cycles

- dyeings can be performed in standing baths

- saves time, water and energy.
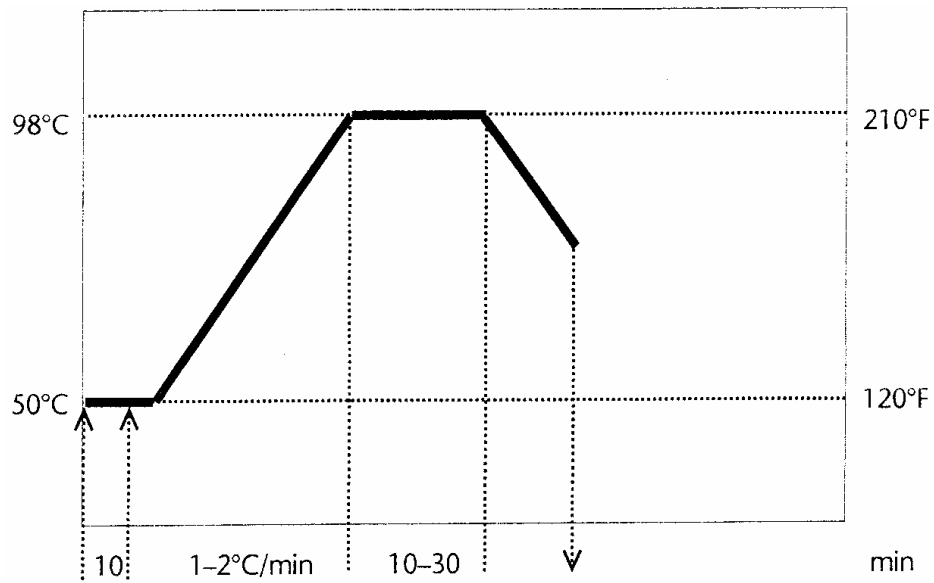
A	0.5 g/l	CIBAFLOW CIR or ALBEGAL FFA
	1 g/l	MIRALAN Q
	1.5%	MIRALAN TOP
	x%	Formic acid 85%
	pH 4.0–4.5	
B	y%	LANASET dyes

Note*: For pale shades a combination of 1.0% MIRALAN TOP with 0.5% ALBEGAL SET is recommended to improve levelness. MIRALAN TOP also improves dyeing rate at 85℃.

Procedure for yarn and piece dyeing

A	0.5 g/l	CIBAFLOW CIR or ALBEGAL FFA
	1 g/l	MIRALAN Q
	1–1.5%	ALBEGAL SET
	5–1 0%	Glauber's salt anhyd.
	1 g/l	Sodium acetate cryst.
	x%	Acetic acid 80%
	pH 4.5	
B	y%	LANASET dyes

The pH of the dye bath can be set with 3–5 g/l CIBATEX AB-45 instead of using acetic acid and sodium acetate/

Shading

LANASET dyeings are highly reproducible. All LANASET dyes can be used for shading. As a rule there is no need to top up with chemicals. Before the shading dye is added, the dye bath should be cooled to 75–80℃/167–176℉. For loose wool and stubbing, the additions can be made with steam off.

Correction of faulty dyeings

Dyeings that have turned out too deep or slightly unlevel can be weakened by 10–15% or levelled by treating in a fresh bath for 30 minutes at the boil with:

	2 %	ALBEGAL SET
	10%	Glauber's salt anhyd.
	X%	Acetic acid 80%
	pH 6–7.	

Before re-dyeing cool dye bath to 60℃ and adjust with acetic acid to pH 4.5.

Shade weakening by 30–40% can be achieved by treating in a fresh bath for 30 minutes at the boil with:

4%	TINEGAL W
10%	Glauber's salt anhyd.
X%	Acetic acid 80%
pH 6–7.	

To remove Ciba TINEGAL W residues and improve rubbing fastness before redyeing, the goods should be treated (after rinsing) with 2% Ciba IRGASOL DAM for 10 minutes at 40℃/104℉ and rinsed again. Redye in a fresh bath.

Note: LANASET Violet B, Blue 2R and Blue 5G can only be weakened marginally.

Moth-proof and beetle-proof finishing

Ciba MITIN FF gives lasting protection against clothes moth, fur and carpet beetle larvae. The effects are fast to light and washing. The finish can be applied in the dye bath by adding 1–1.5% MITIN FF high concentration or 2.5–4% MITIN FF liquor before all other chemicals.

Sulphonated 1:2 metal complex dyes

Lanasyn S dyes

Lanasyn S dyes are sulphonated 1:2 metal complex dyes, which are distinguished by their high colour strength, high standard of fastness and their wide scope of application with regard to types of fibre, articles and range of processes. Lanasyn S dyes are suitable for dyeing wool, silk and polyamide fibres as well as their component in blends with other fibres. Particularly prominent qualities are:

- outstanding solubility

- excellent build up power, high processing fastness properties. very high end-use fastness properties

- HT resistance

- good combinability.

How to dissolve the dyes

Lanasyn S dyes are available in powder form. They are pasted with soft, cold water then boiling water is poured over the paste. In high concentrations brief boiling may be an advantage.

Lanasyn S dyes exhibit excellent solubility (see data in illustration section). The addition of special auxiliaries is therefore unnecessary.

Remark: The Lanasyn S dyes are stable in hard water. If the works' water requires the addition of sequestering agents, inorganic complex formers such as Calgon T (Benckiser, FRG) can be used without any problems.

Scope of application

Because of their high standard of fastness as well as their well-balanced dyeing behaviour, the Lanasyn S dyes can be applied to wool in all forms on all the usual machines:

Scope of application ▼ / Make up ▶	Flock	Yarn	Tops	Piece goods[1]
Men's outerwear	+	+	+	+[2]
Ladies' outerwear	+	+	+	+
Knitwear[3]	+	+	+	+
Uniform cloth[4]	+	+	+	+
Home textiles, furnishing fabrics	+	+	+	+
Carpets, floor coverings	+	+	+	○

[1] only for deep shades
[2] depending on the article
[3] for Superwash wool preliminary trials are advisable
[4] note the potting fastness

Pretreatment

As is well known, the levelness and fastness of dyeings can be impaired by residues of fat and spinning oils. The material to be dyed must therefore be prepared with adequate care.

Detailed information and guide recipes are given in Brochure No. 9391/74 *The Preparation and Bleaching of Textiles.*

Dye selection

The Lanasyn S dyes are individually characterised in the illustration section, where the optimum fields of application are indicated.

Combinability

Lanasyn S dyes are all combinable with each other. For bright fashion shades they can also be combined with 9 Sandolan N, Sandolan Milling N and Lanasyn Brilliant dyes. With these, a large range of shades with a high standard of fastness can be covered.

Chrome resistance

Lanasyn S dyes can be applied in dye baths containing chrome salts. With yellow, brilliant blue and green shades, the self-colour of the chrome salts may affect the dyeings. Lanasyn S dyes can be used as shading elements with Metomega Chrome dyes in the Metomega Chrome dyeing process. The possible changes in shade which result are indicated in the illustration section.

Dyeing behaviour

Lanasyn S dyes are applied from a neutral to weakly acid bath (pH 5–7). The ideal initial pH lies between 6.8 and 6.3, depending on the depth of shade. Depending on the pH of the water, an addition of acetic acid may be necessary for complete exhaustion of the bath.

Chemicals

Lyogen SU Liquid

This slightly fibre-substantive, anionic product provides for perfect root-tip distribution of the dye (and thus prevents skitteriness of the dyeings). It is especially suitable for Lanasyn S dyes, since the normally good levelling behaviour of these dyes is improved even further.

Lyogen SU Liquid has the same effect when dyeing with the Sandolan Milling N dyes, which are suitable for use as shading elements.

When the pH is lower than 4 to 4.5, the effect of Lyogen SU Liquid is distinctly weakened (in exceptional cases, such as when using acid-dyeing shading elements).

Lyogen SMK Liquid

This dye-substantive, amphoteric product is primarily effective as a levelling agent and promotes dye migration. It also improves the root-tip distribution. When added in large amounts this product has a distinct retarding effect.

Exhaust method

Flock and tops

Dye bath additions: x% Lanasyn S dye

3% ammonium sulphate

pH 6.3–6.8 (adjusted with acetic acid if necessary)

Raise the bath temperature evenly in 30 to 40 minutes from 50°C to 95–100°C. After 15–40 minutes dyeing at this temperature (depending on the depth and the machine), cool and rinse. For dark shades the dye bath can be exhausted with acetic acid at the fixation temperature if necessary.

Yarn, woven and knitted goods

Dye bath additions: x% Lanasyn S dye

3% ammonium sulphate

2% LyogenSU Liquid

pH 6.3–6.8 (adjusted with acetic acid if necessary)

According to the machine and depth of shade, raise the bath temperature from 50°C/122°F by 0.5–2°C/1–4°F per minute to 95–100°C/203–212°F. Depending on the depth of shade, fix at this temperature for 15–45 minutes. Finally, cool and rinse.

Before adding shading elements it is advisable to cool the dye bath to 60–800°C/140–176°F.

Dyeing program
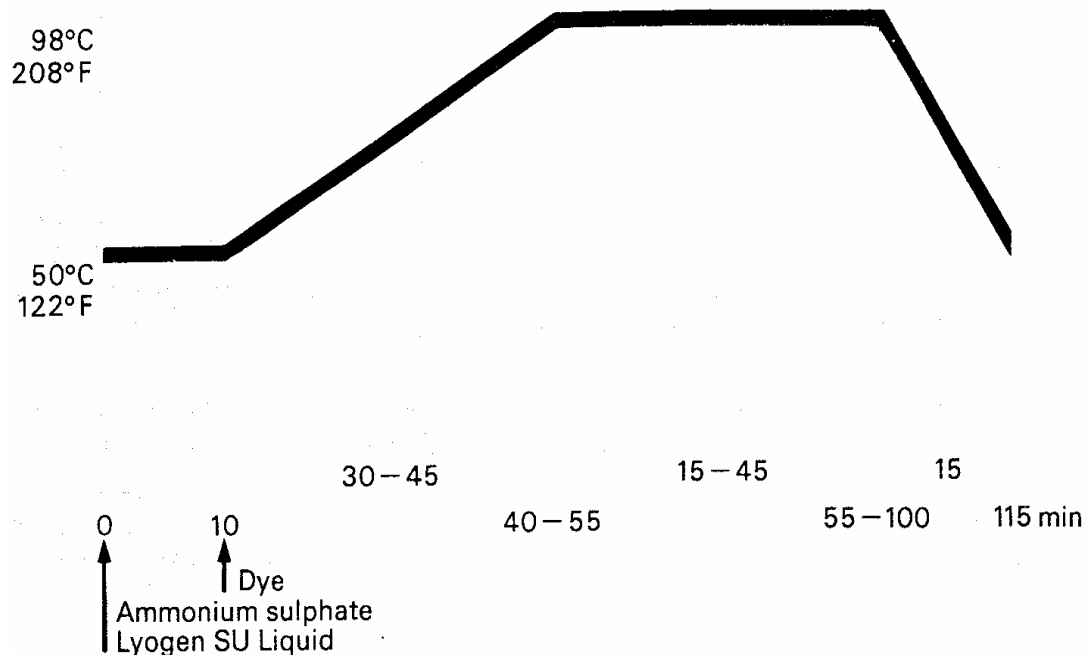
Dyeing in a standing bath

In wool dyeing plants it is a well known technique to use the exhausted dye baths again. The wool degradation products act as protective colloids and thus improve the spinning properties of the wool. A further advantage is the saving in water and energy, particularly with large batches. Dyeing in a standing bath is used mainly for flock and tops; for yarn and piece goods this method has no great significance.

Behaviour of the Lanasyn S dyes

Under the recommended dyeing conditions of pH 5.5–6 without the addition of chemicals, Lanasyn S dyes exhaust in pale to medium shades up to at least 95%, so that the re-use of dye baths offers no dyeing problems.

If, in the case of delicate articles, Lyogen SU Liquid is added to improve the skitteriness, the concentration of the auxiliary agent is reduced by about 50% per dyeing and, together with the usual liquor loss, must be replaced. If this is not done, changes in the levelling behaviour of the dyes may occur during the dyeing of further batches.

Dyeing at 80–85° C

1:2 metal complex dyes, including sulphonated products, are in general not suitable for dyeing at temperatures below 95℃. This results in weaker, appreciably less level dyeings. If, however, for technical reasons it is only possible to dye at a maximum temperature of 85℃, an addition of 3% Lyocol BC Liquid produces a distinct improvement in depth. The appearance of the goods is, nevertheless, not as even as a dyeing carried out at 95–100℃.

Correction of off-shade dyeings

If the dyeing is too dark, it can be lightened by boiling for 30–60 minutes with:

1–4% Lyogen WD liquid

20% Glauber's salt calc.

(pH 6 adjusted with acetic acid).

Lyogen WD is highly dye-substantive and should not be used as a levelling agent. The root/tip distribution is not improved.

Before redyeing it is advisable to wash the material for 15 minutes at 500℃/122°F with 1 ml/1 8 Sandopan TFL Liquid.

Dyeings that are slightly uneven can be levelled out by boiling for 30–60 min at pH 6 with

1–3% Lyogen SMK Liquid

20% Glauber's salt calc.

5.2   Dyeing wool with reactive dyes

Reactive dyes for wool dyeing are offered by a number of suppliers, including Drimalan F dyes from Clariant, the Hostalan range from Hoechst and the Lanasol range from Ciba. These reactive dyes are especially suitable for dyeing machine-washable treated wool.

General

The LANASOL range consists of sulpho-group-containing reactive dyes, which have been especially developed for wool dyeing. They contain one or two bromo-acrylamide reactive

groups, which form a covalent bond with the nucleophilic groups of the wool's amino acids during the dyeing process, resulting in outstanding wet fastness properties.

LANASOL dyes are applied from a weakly acid bath in the presence of ALBEGAL B. They are suitable for untreated and shrink-resist-treated, for example, chlorinated and machine-washable, wool in all its forms, especially loose stock, stubbing and yarn. They can also be used on silk.

Outlets

The LANASOL range is suitable for dyeing wool as loose stock, stubbing, yarn and piece for the following outlets:

- untreated, shrink-resist-treated and machine-washable wool

- women's and men's outerwear, uniforms

- blankets and upholstery

- knitted and woven fabrics

- fully fashioned knitwear

- floor coverings

- articles made from fine animal fibres, for example, cashmere, mohair.

Main characteristics and benefits

Properties	Customer benefits
Broad shade range	Brilliant shades with highest wet fastness
	Brilliant and restrained combination shades at all depths
	Navy and black shades with outstanding wet fastness
Maximum wet fastness properties	Suitable for all end products
	Suitable for shrink-resist-treated wool
	'Superwash' standard attainable
	Highest fastness to processing
	Fastness level similar to that of chrome dyes
High exhaustion and fixation	Excellent reproducibility
	Minimal effluent pollution
Metal-free	No metal in waste water or activated sludge
	Reliable replacement of chrome dyes
	Suitable for Oeko-Tex Standard 100

Pretreatment

Preliminary washing

If the goods are soiled by grease, oil, spinning waxes or dirt, it is advisable to wash them before dyeing. This can be done in the dyeing machine, using soft water.

Suggested recipe:

0.5–2 ml/1 ULTRAVON CN or TINOVETIN JUN h.c.

0–2 g/l INVATEX CS

<u>y g/l</u> ammonia or soda ash

pH 7–9

20–40 min at 40–60℃

rinse warm and cold.

In some cases the addition of electrolyte, for example, up to 5 9/1 sodium sulphate, can assist the removal of mineral oil lubricants.

Bleaching / fluorescent whitening

Wool can be bleached at all stages of processing using conventional dyeing equipment.

Oxidation bleaching

The most commonly used bleaching agent, hydrogen peroxide, is applied under alkaline conditions using pyrophosphate as pH stabiliser. To minimise wool damage, the specified pH and temperature conditions should be strictly observed.

Suggested recipe:

0.5–1 ml/l	ULTRAVON CN
1–2 g/l	Tetrasodium pyrophosphate
0–1.5 g/l	AVIVAN SFC
15–30 ml/l	Hydrogen peroxide 35%
<u>y 9/1</u>	Ammonia or soda ash

pH 9–9.5

2–4 hours at 50℃

or

Start at 50℃ and leave to cool down.

Overnight drain, rinse and sour off to pH 5.5.

A phosphate-free alkaline bleaching method using stabiliser TINOCLARITE BAC gives whites that are superior to those obtained by stabilising with phosphate:

4 g/l TINOCLARITE BAC

15–30 ml/l hydrogen peroxide 35%

60 minutes at 45℃

Drain, rinse and sour off to pH 5.5.

Reduction bleaching

Reduction bleaching using stabilised hydrosulphite can be performed as a single process where full bleaching is not required or as a treatment to follow hydrogen peroxide bleaching. In the latter case, reduction bleaching will give an improved, neutral white, generally with better light fastness than that attained with peroxide bleaching alone.

Suggested recipe:

0.5–1 ml/l ULTRAVON CN

2–3 g/l CLARITE PS

X% fluorescent whitening agent

1–1.5 hours at 50–60℃

Rinse and add 0.5 mi/1 hydrogen peroxide 35% to the final rinsing bath to remove residual sulphurous compounds.

If required, a fluorescent whitening agent (FWA) can be added to the reduction bleaching bath. The following FWAs can be used, depending on required shade.

FWA	Required amount	pH	Shade
UVITEX NFW liq.	0.5 - 2 %	5-6	blue-violet
UVITEX CF liq. 200 %	0.5 - 2 %	6-7	red
UVITEX BHT liq. 115%	0.75 - 3 %	7	neutral blue

Dye selection

Both brilliant and dull shades at all depths can be achieved with the LANASOL ALBEGAL B system. Using either brilliant LANASOL dyes as a basis for self shades or the LANASOL trichromatic system, Yellow 4G, Red 6G, Blue 3G, all fashion shades can be obtained with high wet and light fastness properties.

Recommendation for combination shades

Trichromatic dyes

A wide shade range can be covered with the trichromatic dyes, LANASOL Yellow 4G, Red 6G and Blue 3G. Dyeings have high light fastness and very good fibre levelness.

For darker shades, LANASOL Orange RG or Scarlet 3G can be used as yellow and red components respectively.

Briqht shades

Bright shades are best produced with single dyes or a combination of two similar bright dyes and if necessary, shaded with a trichromatic component.

Scarlet and red shades

Bright, full scarlet and red shades with outstanding wet fastness are obtained with bireactive LANASOL Scarlet 3G, Red 2G and Red GN.

Violet shades

For bright and fast violet shades, LANASET Violet B, if necessary shaded with LANASOL dyes, can be applied by the same dyeing method as that used for LANASOL dyes.

Turquoise and green shades

Bright turquoise and green shades with good light and wet fastness properties are attainable with LANASOL Blue 8G-01 150%, using LANASOL Yellow 4G and/or LANASOL Blue 3G as shading component. For shrink-resist-treated wool, CIBACRON Turquoise P-GR 150% should be used instead of LANASOL Blue 8G-01 150%. On tippy-dyeing wool or heterogeneous wool mixtures, 5–10% NEOLAN Green E-B 400% in addition to the respective LANASOL or CIBACRON dye may improve fibre levelness.

Navy and black shades

LANASOL navy and black dyes can be shaded with the other LANASOL dyes for full navy or black shades. They cannot be used for blue or grey shades or as trichromatic dyes.

Dyeing

Dyeing chemicals

Penetration accelerants

CIBAFLOW CIR or ALBEGAL FFA is added to the dye bath to de-aerate and rapidly wet out the goods. These products also have a foam-suppressing effect.

Levelling agent

ALBEGAL B is amphoteric and has affinity for both dye and fibre. It promotes exhaustion, fibre and surface levelness, and assists penetration of the dyes. With pale and medium shades on yarn and piece goods, 10–15% Glauber's salt anhyd. promotes surface levelness by slowing down the rate of dye uptake. At 11 quor ratios from 8:1 to 30:1, 1–2% ALBEGAL B is added, depending on the shade depth desired. For darker shades, the higher amount of ALBEGAL B is recommended in order to improve exhaustion.

Turquoise and green shades based on LANASOL Blue 8G are dyed with 1.5–2% ALBEGAL B. On heterogeneous wool mixtures or shrink-resist-treated wool these turquoise and green combinations and also CIBACRON Turquoise GR gran. 150% are preferably applied by adding 1% ALBEGAL SET to the standard dyeing recipe.

ALBEGAL B should not be used in conjunction with anionic auxiliaries, because these impair its effectiveness.

Wool care product

MIRALAN Q improves the quality of the wool at all stages of processing. It reduces felting and setting during dyeing and has a lubricating effect. Carding and spinning properties of loose material are improved. In package dyeing, flattening on crossover points is reduced and bulk increased. In piece dyeing, running marks and felting are prevented.

Dissolving the dyes:

- Paste the dye cold with soft water.

- Add hot water (60–90℃) and boil up briefly with live steam if necessary.

- Stir thoroughly (with rapid stirrer if necessary).

Auxiliaries and chemicals should not be added during dissolving.

Procedure for yarn and piece dyeing
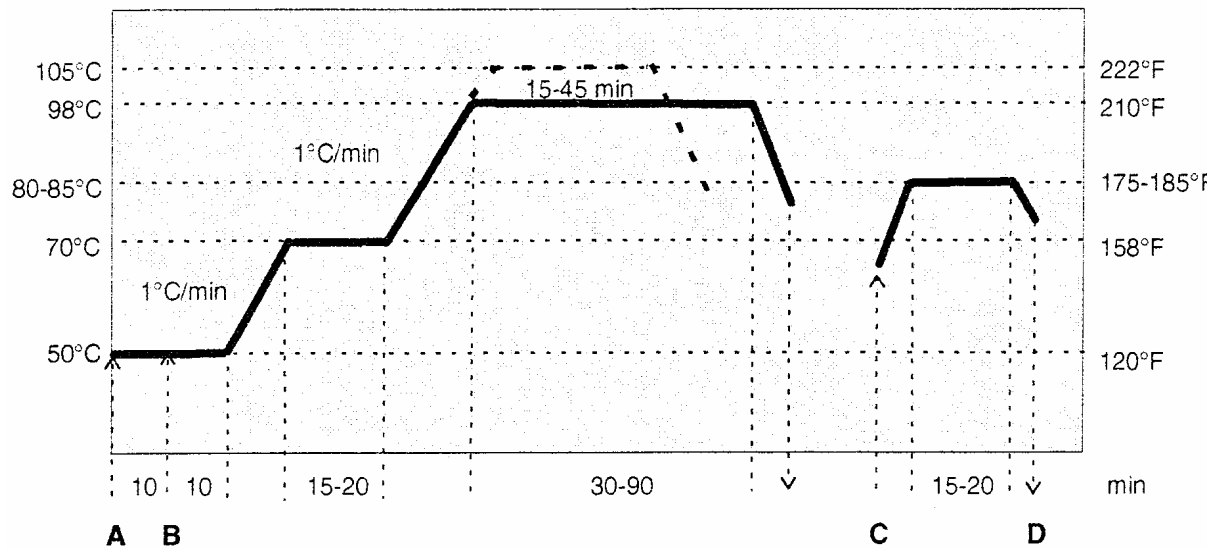
A	0.5 g/l	CIBAFLOW CIR or ALBEGAL FFA
	1 g/l	MIRALIN Q
	10–5%	Glauber's salt anhyd.
	1–2%	ALBEGAL B
	4%	Ammonium sulphate
	x%	Acetic acid 80%
	pH 7.0–4.5 (see pH curve)	
B	y%	LANASOL dyes
C	Preferably in a fresh bath at 80–85°C	
	-z% ammonia or soda ash or sodium bicarbonate	
	pH 8.0–8.5	
D	Rinse warm and cold.	
	Acidify with 1% formic acid 80% in the final rinsing bath.	

Procedure for shrink-resist-treated and machine-washable wool
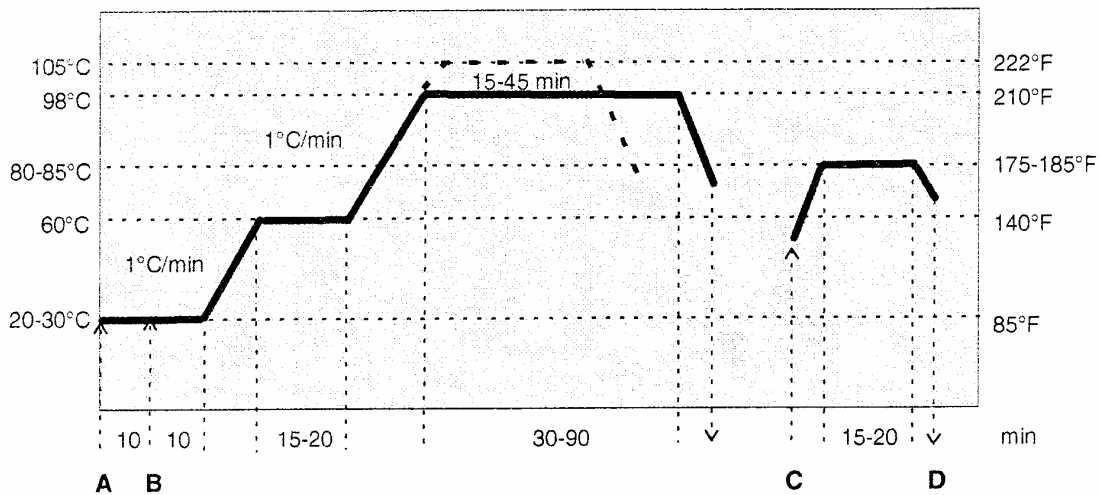
A   0.5 g/l   CIBAFLOW CIR or ALBEGAL FFA

           1 0–5 %   Glauber's salt anhyd.

           1–2 %   ALBECAL B

           4%   ammonium sulphate

           x%   acetic acid 80%

           pH 7.0–4.5 (see pH curve, top line)

B   y%   LANASOL dyes

C   Preferably in a fresh bath at 80–85°C

           z %   Ammonia or soda ash *or* sodium bicarbonate

           pH 8.0–8.5

D   Rinse warm and cold.

           Acidify with 1% formic acid 80% in the final rinsing bath.

Notes: In critical cases, an addition of 1% ALBEGAL SET to the standard dyeing recipe improves levelling.

Treatment time at different dyeing temperatures

Exhaustion by no means marks the end of the dye-fibre reaction. The treatment time required depends on the amount of dye and on the temperature.

Dye	Treatment time at dyeing temperature		
	98°C	85°C	105°C
0.5 %	30 min	45 min	15 min
1 %	40 min	60 min	20 min
1.5 %	50 min	75 min	25 min
2 %	60 min	90 min	30 min
3 %	75 min	120 min	35 min
>4 %	90 min		45 min

Dyeing pH

As with wool dyes applicable under mildly acid conditions, the pH of the dye bath depends on the depth of shade and on the affinity of the wool fibre. Fibre affinity is generally increased by shrink-resist-finishes like chlorination or PMS-treatment and in particular by machine-washable finishes such as chlorine/Hercosett. The graph below shows the recommended dyeing pH for the total amount of dye used. The pH must be checked *before* the dye is added.
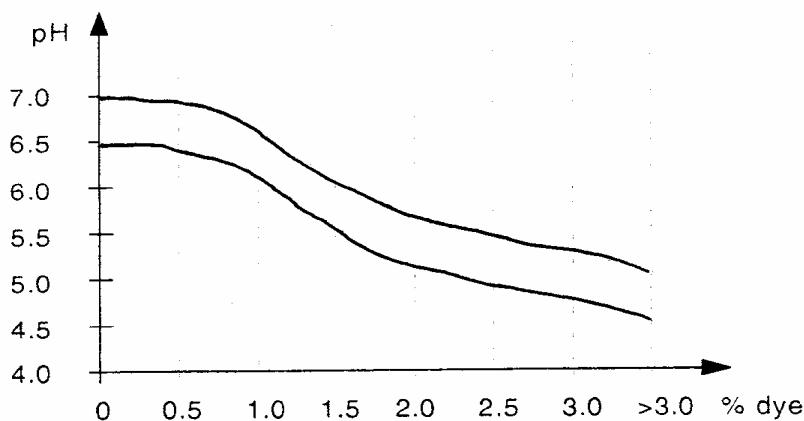
- Dyeing untreated wool with LANASOL dyes and LANASET Violet B: within the given bandwidth.

- Dyeing shrink-resist-treated and machine-washable wool with LANASOL dyes, LANASET Violet B and CIBACRON Turquoise CR gran. 150%: upper curve.

If the pH range for the given shade is maintained and precisely measured (pH meter or special indicator paper) the dye will exhaust uniformly and evenly to give a level shade. With yarn and piece goods, or alkaline process water, or if there are alkali residues on the goods, it is advisable to adjust the dye bath pH with a buffer, for example, ammonium sulphate/acetic acid. When dyeing at pH 5.5–4, sodium acetate/acetic acid can also be used to adjust the pH.

If the wool still contains residues of acid, for example, from an acid shrink-resist-treatment or carbonising, the acid should be buffered with 5–8% sodium acetate cryst. or the pH adjusted to 9 with ammonia before setting the dye bath pH.

LANASOL black dyes

LANASOL black dyes are preferably applied as follows:

0.5 g/l	CIBAFLOW CIR or ALBEGAL FFA
1 g/l	M I RALAN Q
x%	acetic acid 80% and/or formic acid 85%
2%	ALBEGAL B

pH 4–4.5

The bath should also contain 1 g/l IRGASOL NA to avoid possible soiling of the machine.

Brilliant pale shades dyed at 85°C.

Brilliant pale shades are dyed at 85°C in the presence of an oxidising agent (hydrogen peroxide) or a mild reducing agent (ERIOCLARITE B). With either method, separate preliminary bleaching is often unnecessary.

Procedure with hydrogen peroxide:

Five to 10 ml/l hydrogen peroxide 35% is added to the bath together with the dyeing chemicals. After 20 minutes at 30℃, the dye is added and the temperature is raised to 60℃ at 1℃/min. The goods are treated at that temperature for 30 minutes, the bath is heated to 85℃ over 10 minutes and dyeing carried out at that temperature for 30–40 minutes. The bleaching effect can be intensified by an addition of l g/l ERIOCLARITE B after 15 minutes at 85℃.

Procedure with ERIOCLARITE B

One g/l ERIOCLARITE B is added to the dye liquor along with the other dyeing chemicals.

Finishing and neutralising

Pale dyeings are rinsed and if necessary soured off with 1% formic acid 85%.

Dyeings produced with about 1.5% dye and upwards (LANASOL Orange RG, Scarlet 3G, Red GN and Red 2G on untreated wool in amounts above 2.5%) should be neutralised to remove any dye not covalently bound to the fibre.

Neutralising with ammonia, soda or sodium bicarbonate

Add dilute ammonia or a solution of either soda or sodium bicarbonate to a fresh bath.

x% ammonia or *soda* or sodium bicarbonate pH 8–8.5

15 minutes at 80–85℃

Rinse warm and cold.

Acidify with formic acid.

Cool liquor sample to room temperature before measuring pH.

Shading

LANASOL dyeings are highly reproducible. All LANASOL dyes can be used for shading. As a rule there is no need to top up with chemicals. If large amounts of shading dye are required, 0.5% ALBEGAL B should be added.

The bath is cooled to about 60℃ by running in cold water. When the goods are at the same temperature throughout, the dye is added. After 10–15 minutes, the bath is heated evenly to 85℃ and the goods are treated at that temperature for 20–40 minutes. If necessary, they are then neutralised in the usual way.

Correction of faulty dyeings

The irreversible bond linking the dye to the fibre makes it impossible to even up unlevelled dyeings or weaken shades that have turned out too deep. Faulty batches in pale and medium shades are best redyed to a dark shade or black. If the goods are redyed with 1:2 metal complex dyes, 1% ALBEGAL A should be added to the dye bath.

Stripping

Faulty dyeings can be stripped only by destroying the dyes with a hydrosulphite reduction treatment in a bath containing formic acid. Preliminary trials are essential, because not all LANASOL dyes are completely stripped. Goods that have been redyed generally have a harsh handle, and this can be corrected in the final rinsing bath with 1–2% SAPAMINE WL at 30–40℃.

Moth-proof and beetle-proof finishing

MITIN FF gives lasting protection against clothes moth, fur and carpet beetle larvae. The effects are fast to light and washing. The finish can be applied in the dye bath (add MITIN FF before ALBEGAL B). The best protection is achieved if MITIN FF is applied after neutralising.

1–1.5% MITIN FF high conc.

or

2.5–4% MITIN FF liq.

pH 4–5

70–90℃ for 30 minutes

LANASOL CE

Wool dyeing

General

LANASOL CE metal-free reactive dyes have been especially developed for wool dyeing. With their excellent wet fastness properties and high cost effectiveness, LANASOL CE dyes are especially suitable for deep shades and for replacement of afterchrome dyes.

Main characteristics and benefits

Properties	Customer benefits
Metal free	No handling of dichromate No metal in waste water or activated sludge Suitable for Oeko-Tex Standard 100
Maximum wet fastness properties	Suitable for all end products 'Superwash' standard attainable Highest fastness to processing Dependability for the dyer Ideal replacement for chrome dyes
High exhaustion and fixation	Excellent reproducibility Highest dependability in dyeing Minimal effluent pollution
Application in the isoelectric	Maximum preservation of wool quality
Range of wool	Improved spinning yield = cost savings Fewer end breaks = cost savings Softer handle than chrome dyed wool
Can be shaded with LANASOL dyes	Component of a reliable dyeing system Highest dependability in dyeing Wide shade range Low inventory
Cost-effective dyes	Ecological, progressive dyeing without additional costs Cost-competitive with chrome dyes

Uses

LANASOL CE dyes are suitable for exhaust dyeing of untreated, shrink-resist-treated, for example, chlorinated and machine-washable, wool in all forms, especially loose stock, stubbing and yarn.

Dyeing

LANASOL CE dyes are applied by the standard LANASOL dyeing procedure and can be shaded with other LANASOL dyes.

LANASOL CE in relation to the other LANASOL dyes

The LANASOL CE trichromatic system is based on the same proven (X-bromo-acrylamide reactive group as the classic LANASOL range).

With its excellent wet fastness properties and high cost effectiveness, the LANASOL CE trichromatic system is especially suitable for deep shades.

LANASOL NAVY CE and LANASOL BLACK CE are the basis for economical navy and black shades, which can be shaded with all other LANASOL or LANASOL CE dyes.

Yellow CE   Yellow component of the LANASOL CE trichromatic system. Basis for olive and brown shades.

Red CE   Red component of the LANASOL CE trichromatic system. On its own for brilliant deep red shades.

Blue CE   Blue component of the LANASOL CE trichromatic system. Basis for bottle greens in combination with LANASOL Yellow CE or Yellow 4G. Basis for light navy shades.

Navy CE   Cost-effective navy dye with excellent wet fastness. Ideal replacement for all chrome navy shades.

Black CE   Highly cost-effective black with excellent wet fastness. Shade close to that of ERIOCHROME Black tfd.

5.3   Dyeing wool with chrome dyes

General

Eriochrome dyes contain groups capable of complexing with various metals. These are applied from a weakly acid bath to form a stable, insoluble complex (chrome lake) on the fibre with trivalent chromium, using as active reagent chromate ions liberated by potassium dichromate under the action of the acid.

The most widely used dyeing method is the after-chroming process, which also gives the best fastness properties. The dye is first applied from a weakly acid bath then a hexavalent chromium salt, usually potassium dichromate, is added to the bath and the complex forms on the fibre.

In the one-bath chroming process the dye bath is set with selected Eriochrome dyes, potassium dichromate and ammonium sulphate. This method has lost some of its former importance because the fastness properties obtained are somewhat on the low side.

In the pre-chroming process the wool is first mordanted with potassium dichromate and acid, after which it is dyed in a fresh bath with selected Eriochrome dyes.

Selected Eriochrome dyes are also suitable for continuous dyeing and melange printing on stubbing.

Properties

- Good levelling and penetration.

- Can be applied with selected textile chemicals below the boil to minimise fibre damage.

- Suitable for high temperature application.

- Generally good reservation of cotton, viscose and acetate effect yarns.

- Good to very good light fastness.

- Very good wet fastness, even in dark shades.

Uses

- Stubbing, loose stock, yarn and piece goods for ladies' and men's outerwear.

- Stubbing, loose stock, yarn and piece goods for uniforms.

- Stubbing, loose stock and yarn for knitting.

- Loose stock and yarns for floor coverings.

The choice of dyes in each case will depend on the fastness properties and characteristics required of the dyed goods.

Notes on dyeing

Scouring

Good dyeings cannot be obtained unless the material has first been thoroughly scoured to remove grease, soap and lubricants which could lead to unevenness, stains or sub-standard fastness properties.

Water

It is best to use soft water. Hard water or water containing salts of heavy metals such as iron and copper is detrimental as such, but will give no trouble if a chelating agent such as 0.1–0.5 g/l lrgalon ST is added.

Liquor ratio

The recipes given for the individual methods are based on a liquor ratio of 20:1. If other liquor ratios are used, the concentrations of acids, salts and so on will have to be altered accordingly.

Potassium dichromate

A given amount of potassium dichromate and acid is required to ensure that the chrome lake is properly formed on the fibre. In general the amount used (0.25–1.5%) is half the amount of 100% strength dye.

A number of Eriochrome dyes can be developed with considerably smaller amounts of potassium dichromate without adversely affecting either fastness properties or shade. This is a particularly valuable feature as regards reducing water pollution. Moreover, the treatment does not impair either handle or elasticity of the material and has a beneficial effect on the spinning properties of loose stock and stubbing.

The minimum requirement of potassium dichromate is given in the fastness tables as a percentage by weight of the amount of dye applied.

As a rule, the following minimum amounts of potassium dichromate and acid are recommended:

0.25% potassium dichromate

1% formic acid 85%

or

1% sulphuric acid 96% pH about 4.

Chroming in a poorly exhausted dye bath leads to unsatisfactory fastness. If for some reason exhaustion is unsatisfactory, it is an advantage to chrome in a fresh bath set with:

X% potassium dichromate

1.5–2% formic acid 85%

or

1–1.5% sulphuric acid 96%

30–45 min at the boil

Dissolving the dyes

To obtain good dye solutions:

- Paste the dye thoroughly with cold water.

- Add boiling water.

- Stir thoroughly (using a high-speed stirrer if necessary)

- Boil up briefly with live steam if necessary.

- Add to the dye bath through a fine sieve or filter Eriochrome Black T fd. 200% and Eriochrome Black AZ paste.

- Add warm water (boiling up not essential).

- Add to the dye bath.

or

- Strew in (if machine is suitable).

Method 11

Dyeing below the boil

By its very nature, dyeing with chrome dyes is one of the processes least gentle to the wool fibre. The damage caused to the fibre can, however, be minimised by lowering the dyeing temperature. For good batch-to-batch shade reproducibility it is essential to dye in machines with automatic temperature control.

Notes

Amount of acid

For optimum dyeing conditions, the amount of acid should be adjusted to local requirements. The acid concentration is correct when the dye exhausts slowly and completely. When shades other than black are being dyed, the full requirement of acid can be met with formic acid, which is added at the outset, and it is essential to use dyeing equipment with efficient liquor circulation.

Temperature

The chroming temperature of 90℃/195℉ – 92℃/198℉ gives good shade development and fastness properties. Preliminary trials are advisable because the shade and fastness properties obtained at this temperature may differ slightly from those obtained by chroming at the boil.
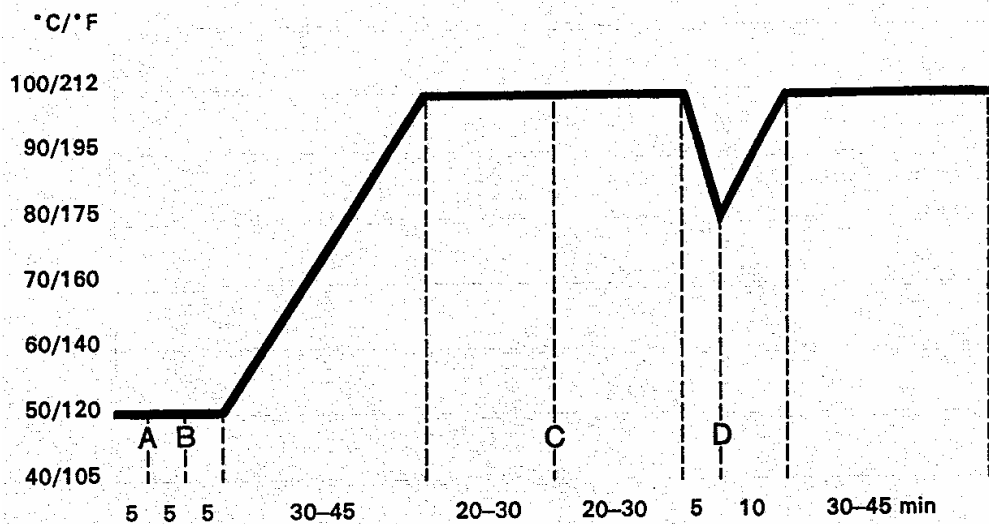
Auxiliaries

Albegal B (amphoteric) can be used to advantage in this method where it improves the levelness of the dyeing and promotes shade development.

Albegal C is recommended as de-aerating agent and antifoam.

With black dyes, *lrgapadol P* promotes dye exhaustion and improves the rubbing fastness of the dyeings.

Method I
Dyeing at the boil and after-chroming

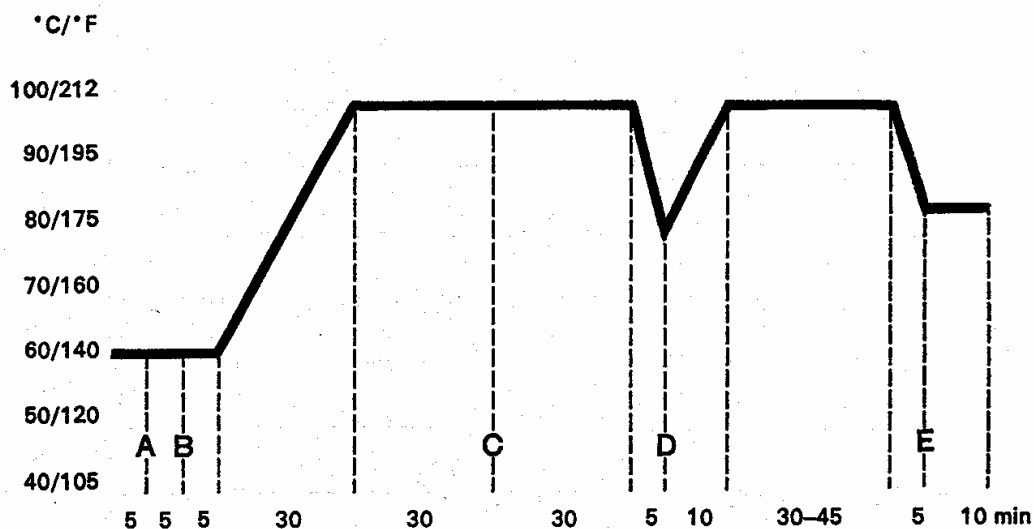Dyeing cycle

Recipe

A 1 –2 % acetic acid 80%
   5   % Glauber's salt anhyd.
            if necessary
   0.2 –0.5% Albegal A or SW
   0.1   g/l Irgalon ST
   pH about 5

B x   % dye

C 1 –2* % formic acid 85%
   pH about 4

D 0.25–1.5% potassium dichromate

Contemporary wool dyeing and finishing
Dyeing methods for wool: Arthur Fisher

Method Ia
Eriochrome Black T fine disperse 200%

Dyeing cycle

°C/°F

100/212

90/195

80/175

70/160

60/140

50/120

40/105

A B   C   D   E

5 5 5   30   30   30   5 10   30–45   5   10 min

Recipe

A   1 –2 %   acetic acid 80%
               if necessary
     0.1 g/l   Irgalon ST
     0.2–0.5% Albegal A or SW
     ──────────
     pH about 5

B   x   %   Eriochrome Black T fd. 200%

C   1 –2 %   formic acid 85%
     ──────────
     pH about 4

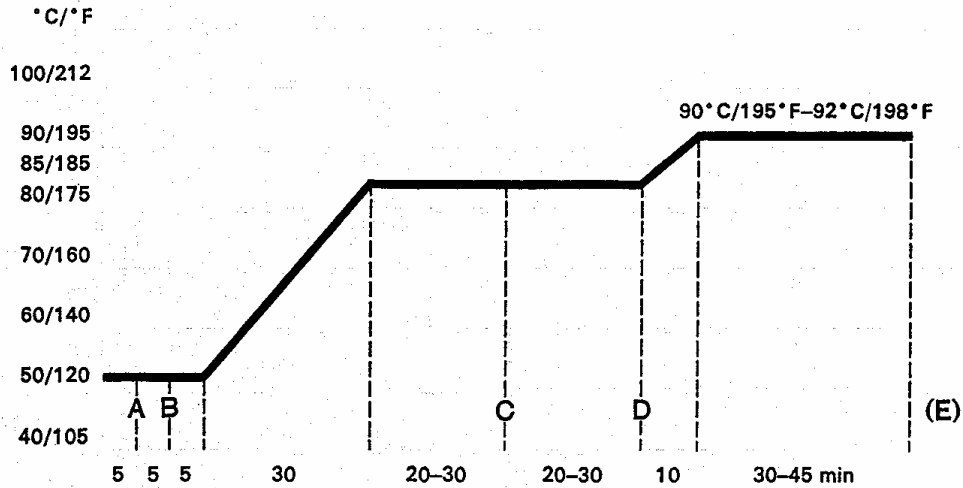D   0.5–1.5% potassium dichromate

E   y   %   ammonia (to remove the yellow-staining
               impurities)
     ──────────
     pH about 8

     rinse
     acidify

Method II
Dyeing below the boil and after-chroming

Dyeing cycle

Recipes

Shades other than black	Black shades

Shades other than black

A   0.1 g/l Irgalon ST
     1.5–2 % acetic acid 80%
     5 % Glauber's salt anhyd.
     0.3% Albegal C
     0.3–0.6% Albegal B
     pH about 5

B   x   % Eriochrome dye

C   1 –2 % formic acid 85%
     pH about 4

D   y   % potassium dichromate

Black shades

A   2   % acetic acid 80%
     0.75% formic acid 85%
   0.2–0.4 % Irgapadol P
     if necessary
     0.1 g/l Irgalon ST
     pH 4–4.5

B   x   % Eriochrome Black

C   1.5–2   % formic acid 85%
     pH 3–4

D   y   % potassium dichromate

(E) to remove the yellow-staining
impurities of
Eriochrome Black T fd. 200%:

z   % ammonia 25%
pH 8

15 min at 80°C/175°F–85°C/185°F

rinse
acidify

5.4　Dyeing wool with 1:1 metal complex dyes

One-to-one (1:1) premetallised dyes are normally dyed at very low pH in the order of 2.0 to 3.0 using sulphuric acid. Prolonged periods at the boil at low pH will produce considerable damage to the wool fibre.

Neolan P dyes and Albegal PLUS a dyeing system for minimal fibre damage

Neolan P dyes are modified azo dyes containing sulpho groups and complexed chromium. As a rule, there is one chromium atom per molecule of azo dye (1:1 metal complex dye). In combination with Albegal PLUS, Neolan P dyes form a specific chemical complex and as a result of this they can be applied at all shade depths at pH 3.5–4, thus ensuring minimal damage to the fibre. Impairment of the physical properties of the fibre (for example, resistance to abrasion, tensile strength and elongation) and chemical characteristics (for example, alkali solubility) is thus negligible. This dyeing system provides high exhaustion of the dye baths, resulting in good shade reproducibility. It is not necessary to buffer the sulphuric acid bound by the wool, as required by the conventional system. The dyeing process is thus shortened; nevertheless wet fastness properties are as good as those obtained by the conventional method with buffering.

Neolan P dyes can be used on carbonised, non-deacidified goods. The pH of the dye bath is raised to 3.5–4 with dilute caustic soda.

The Neolan P range is a small one comprising eight dyes specifically developed to cover virtually the full shade spectrum. Most fashion shades can be obtained cost-effectively and with minimum metamerism with the new trichromatic dyes, Neolan Yellow P, Red P and Blue P, supplemented by Orange P and Blue PA.

Outlets

Suitable for:

- men's and women's outerwear, plain piece-dyed

- loose stock and yarn for floor coverings*

- hand and machine knitting yarns.

Not suitable for severe carpet washing.

Dyeing method

pH of the dye bath

Irrespective of shade depth and form of goods, dyeing is performed at pH 3.5-4, the range that causes least damage to the wool, even on prolonged boiling. The pH is preferably adjusted with formic acid. It should not exceed 4 at the boil.

With carbonised, non-deacidified goods, the pH of the dye-bath is adjusted to 3.5–4 with dilute caustic soda.

Chemicals

Albegal PLUS is a liquid amphoteric auxiliary with affinity for both the dye and the fibre. It has been especially developed for the Neolan Plus system. 2–3% Albegal PLUS is used at liquor ratios of 8:1 to 30:1, irrespective of shade depth. It promotes migration and exhaustion of the dyes, and both fibre and surface levelness. An addition of 6–10% Glauber's salt anhyd is required when dyeing piecegoods or yarn.

Dissolving the dyes

The dye is pasted with cold water, boiling water is added (lowest final temperature 80℃) and the solution thoroughly stirred. If necessary, it can be boiled up briefly. This procedure can also be used for laboratory dyeings.

Shade brightening

If the brightness of a pattern cannot be obtained with Neolan P dyes, combinations of Neolan P with Neolan E or Tectilon dyes can be used.

Neolan Yellow E-3G 180%   Tectilon Yellow 2G 200%

Neolan Red E-2GN 200%   Tectilon Yellow 3R 200%

Neolan Blue E-A 235%*   Tectilon Red 2 B 200% **
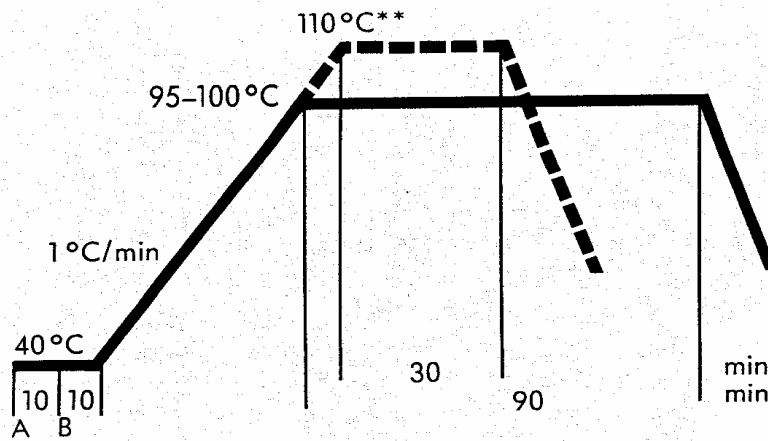
Neolan Green E-B 400%   Tectilon Blue 4R 200%

                              Tectilon Blue 6G 200%

*   Moderate light fastness.

**   Not suitable for dyeing at ll0℃.

Procedure


```
A        0.5– 0.8 g/l  Albegal FFA
         6  –10  %   Glauber's salt anhyd.
         2.5– 5  %   formic acid 85%
         3       %   Albegal PLUS*
         ─────────────
         pH 3.5–4
B        x       %   Neolan P dye
```
* navy and deep shades 2%
**4% Irgasol HTW (dyeing at 110℃)

Notes

Temperature hold

(piecegoods on winch)

15 minuts at 70℃, pale shades 60℃.

Dyeing with Neolan Black P

This dye is applied without Glauber's salt and with 1–1.5% Albegal SET instead of Albegal PLUS. On beam dyeing machines it is applied in the presence of 1–1.5% Albegal SET and 1 g/l lrgasol NA or P (no draining, machine stays clean).

Dyeing at 110°C

An amount of 4% lrgasol HTW must be added to protect the fibre. After the addition of shading dyes, dyeing continues at only 98–100℃.

Fumexol WD

If the goods are being dyed on overflow machines with vigorous liquor circulation, foam can be completely suppressed by adding 0.3–0.6 g/l Fumexol WD (silicone-free antifoam) together with Albegal FFA.

Finishing off

At the end of the dyeing cycle the goods are rinsed thoroughly with warm and then cold water.

Shading

It is advisable to cool the dye bath to 70–80℃ before making shading additions. On winches, about 113 of the bath is dropped and replaced with cold water. An addition of chemicals is not required. If only small additions are required, shading can be carried out with Neolan E or Tectilon dyes with the steam turned off and wet fastness properties will not be impaired.

Correction of faulty dyeings

Dyeings that have turned out too deep or slightly unlevel can be weakened or levelled in a blank bath.

Recipe

4–6% Albegal PLUS

15% Glauber's salt anhyd.

3–5% formic acid 85%

pH 3–3.5

30–45 minutes at 98℃

or

15–25 minutes at 103–C.

Pronounced unevenness or markedly off-shade dyeings can be greatly weakened with minimum damage to the wool by treating in a fresh bath containing:

4–5% sulphuric acid 96%

3–8% Tinegal W

3% lrgasol HTW

30–60 minutes at 98℃

After-treat with:

2% lrgasol DAM

10 minutes at 30–40℃.

Tinegal residues still on the fibre are removed in this process, subsequent redyeing is facilitated and fastness to rubbing improved.

5.5　Dyeing wool with acid dyes

Acid dyes are commonly used to dye wool and wool blends. These are divided into various groups according to the pH at which they are best applied. Depending on which group they fit into they can be applied at pH from as low as 2.0 to 3.0 and as high as 6.0. The wet fastness and light fastness properties vary considerably from one group to another and careful selection is required according to the end use of the article being dyed.

Examples of various classes of acid dyes together with their application procedures may be found at Section 4.5.

6. Dyeing fibre blends

There are three significant reasons for using blends of fibres: economy, physical properties and aesthetics.

- Economy – The partial replacement of expensive fibres, for example, wool with cheaper fibres, can make the market for a fabric wider and increase production volumes.

- Physical properties – The ability to gain some of the advantages of each fibre can be of significant benefit, for example, polyester can contribute strength and wool moisture absorbency to a polyester/wool blend.

- Aesthetics – The attractiveness of the appearance and the handle of the fabric can be improved by the use of blends to give multicoloured fabrics, and combinations of yarns with different characteristics of lustre, crimp, or denier.

Common fibre blends

Polyester/cellulose

Polyester is frequently blended with cotton or viscose rayon in blend ratios from 67:33 to 50:50. The blends are dyeable by exhaust methods and, in the case of woven fabrics, by continuous methods. Preparation prior to dyeing is important and, apart from scouring, possibly in caustic soda, the fabrics are frequently pre-set for 30 to 40 seconds at 180 to 210℃, to minimise dye affinity variations in the fibres.

Polyamide/cellulose

Polyamide/cellulose blends are also frequently encountered to obtain strength and absorbency from their respective components. The polyamide component is often as low as 20%. The blends occur in a wide range of applications including carpets, apparel, work wear, and pile fabrics. Stretch fabrics and garments with textured polyamide are also common.

Polyester/wool

The aesthetic properties of wool are expensive and gain in economy, appearance and durability can be gained by blending it with polyester. The optimum blend is considered to be 35% polyester and 65% wool.

Wool/polyamide

Similar advantages occur in blending wool with polyamide. The blend generally occurs in hand knitting yarns, carpet yarns and stretch apparel fabrics. The percentage of polyamide may be as low as 20%.

Polyacrylonitrile/wool

Polyacrylonitrile/wool blends are encountered in knitwear and soft furnishings.

Acetate/polyamide, triacetate/polyamide

Acetate/polyamide and triacetate/polyamide blends are generally found in filament form in apparel fabrics.

The variety of blends is only limited by the imagination of the fabric designed. Unfortunately, the dyer often struggles as a result of the unfettered rein given to or taken by

the designer. The selection above illustrates only a few of the common blends and will be used later to illustrate the principles described in the next section.

Processing variables with blends

The optimum conditions for an individual fibre may not be able to be used in the dyeing of blended materials. This may be because of the sensitivity of one fibre to the processing conditions normally used by the other or the requirements of the dyeing system for the other fibre if one-bath methods are being used, that is, if both fibres are being dyed simultaneously. The variables that may be affected in these ways are:

- dyeing time.

- dyeing temperature

- dye bath pH.

Dye concentration can be more significant if the dye has affinity for the fibre or stains in heavier depths.

Dye bath auxiliaries may be quite different from those required for the single fibres. Additional auxiliaries may be required for blend dyeing, for example, protective agents for the other fibre, anti-precipitation agents when dyes are incompatible. The liquor and ratio is one variable that will change for a given set of dyeing conditions, because there is not 100% of a fibre present. For example, with 20% polyamide in a blend, a liquor ratio of 15:1 suddenly becomes 75:1. This will have a significant effect on the degree of exhaustion of the dye bath.

The factors that apply to blends and not to single fibre materials are cross staining, dye precipitation and dyeing stages.

Cross staining

Dyeing systems for blends fall into two main categories:

- systems in which one dye has affinity for both fibres, and under appropriate conditions solid shades can be dyed

- systems in which each fibre is dyed with a dye appropriate to it.

In the second case, the extent to which the dyes for one fibre cross-stain the other must be considered.

If cross-staining occurs, the dyer must consider:

- whether the cross-staining is fast and can be left on the fibre

- whether the cross-staining can be removed from the fibre by clearing or scouring treatments

- whether the cross-staining can be limited or prevented by the use of dye bath auxiliaries, dye site blocking agents or the use of two-bath methods rather than one-bath methods.

Dye precipitation

It is possible to dye with dyes of opposite ionic change in the same bath, provided auxiliaries are added to prevent co-precipitation. Similar additions can be made if one or more of the dyes are incompatible with an auxiliary essential to the dyeing of the other fibres. Without such additions, the dyes would precipitate.

One frequent method of limiting precipitation is to add the dyes which would interact in the presence of a dispersing agent, that is, the dyes are allowed to precipitate under controlled conditions, but are kept in dispersion. Provided that the affinity of the dyes for the fibres is greater than their affinity for each other, the dyeing will proceed to a reasonable degree of exhaustion.

Dyeing stages

There are obvious advantages-in time, energy and labour costs if a blend can be dyed in one bath or one continuous dyeing pass. However, unless the dyes used have affinity for both fibres and will give reasonably solid shades, a one-bath method is not always possible. Frequently, pale shades or small proportions of one fibre allow a one-bath method to be adopted when such a method is not generally applicable to the combination.

Provided the compatibility of the components of the dye bath can be reasonably guaranteed, one-bath methods for blends which require two dye types are frequently used. These assume that any cross-staining that occurs is tolerable for the shade, subsequent processing steps and end use required.

The circumstances that require two (or more) baths to be used include:

* incompatible dyeing methods

* unacceptable cross-staining, which must be removed, but cannot be because of the presence of the dye applied to some fibre.

The sequence of dyeing stages must be carefully planned for individual shades, for example, using disperse and 1:2 premetallised dyes on polyester/wool blends and dyeing at temperatures from 100°C to 120°C.

6.1   Dyeing wool/polyester blends

Outlets

PES/wool blended fabrics are mainly used for apparel, particularly for suits. Blending wool with PES makes the fabric cheaper and increases durability and wrinkle resistance. The main outlets are worsted fabrics. The most common blend ratio for PES/WO is 55:45 but a large variety of other blend ratios can also be found in the market. PES/WO blends are dyed in piece form (solid shades) or as yarn on packages (for pattern wovens).

Dyeing systems

There are a number of methods by which wool/polyester blends may be dyed successfully and many dye manufacturers offer products that may be used for this purpose.

The FOROSYN and FOROSYN SE range from Clariant are particularly useful for dyeing blends of wool/polyester from 30% wool and 70% poly to 45% wool and 55% poly. These dyes are mixtures of premetallised and disperse dyes and can be applied to wool/polyester blends using a one-bath method with excellent fastness properties.

Various other options are available for dyeing wool/polyester blends. The polyester component must of course be dyed with Diperse dyes and the wool may be dyed with acid, premetallised or reactive dyes.

Following is a typical application method using a combination of premetallised and disperse dyes applied from a single bath.

All LANASET dyes are ideal for PES/WO blends. They are applied at pH 4.5, which guarantees optimum wool preservation and perfect conditions for the dispersion stability of

TERASIL disperse dyes. LANASET dyes are stable at 120℃ and have excellent migration at this temperature, therefore, they can also be recommended for piece dyeing of PES/WO blends. All LANASET dyes are noted for very good reservation of PES. The selection of dyes follows the same rules as for pure wool.

Excellent technical behaviour during dyeing and good fastness properties make the LANASET dyes the ideal range for dyeing PES/WO blends:

- coverage of a wide range of colours, including brilliant shades

- pale to deep shades are attainable, including navy and black

- one-bath dyeing method

- shade stability at 120℃, with no interference with wool protecting agents

- optimal wool protection

- good overall light and wet fastness.

Important parameters for dyeing polyester and wool blends

Dyeing temperature and time

The most common dyeing temperature is 120℃. At this temperature the selected TERASIL dyes show good build-up on PES and the wool quality is largely preserved if a wool-protecting agent is used (MIRALAN HTP or IRGASOL HTW NEW). The normal dyeing time is 45 minutes; the maximum time limit at 120℃ is 60 minutes. Alternatively, PES/WO blends can be dyed at 106℃. But, in this case, a diffusion accelerant has to be used to achieve sufficient build up on PES. For very fine weaving yarns, where even a small reduction of tensile strength is not acceptable, a maximum dyeing temperature of 115℃ is recommended.

Wool protecting agent

IRGASOL HTW NEW improves the heat resistance and preserves the mechanical and technological properties of the wool fibre at 120℃. The best effects are achieved by using 4% IRGASOL HTW NEW. MIRALAN HTP is free of formaldehyde and achieves similar effects at the same usage level.

Diffusion accelerants

At a dyeing temperature of 120℃ for pale and medium shade depths no diffusion accelerant is required as a rule. For dark shades, especially black and navy, addition of the diffusion accelerant UNIVADINE PB results in better exhaustion and higher reproducibility. At dyeing temperatures below 120℃ UNIVADINE PB is necessary for most types of PES to achieve sufficient build-up. Too much diffusion accelerant can cause blocking effects, depending on the PES type.

Disperse dye selection

The right selection of TERASIL disperse dyes is essential for good results. The main criteria for the selection of TERASIL dyes are stability to reduction and low staining on wool. The recommended TERASIL dyes are shown in the following table. For details see TERASIL pattern card.

Dyeing procedure for WO/PES blends with LANASET and TERASIL dyes
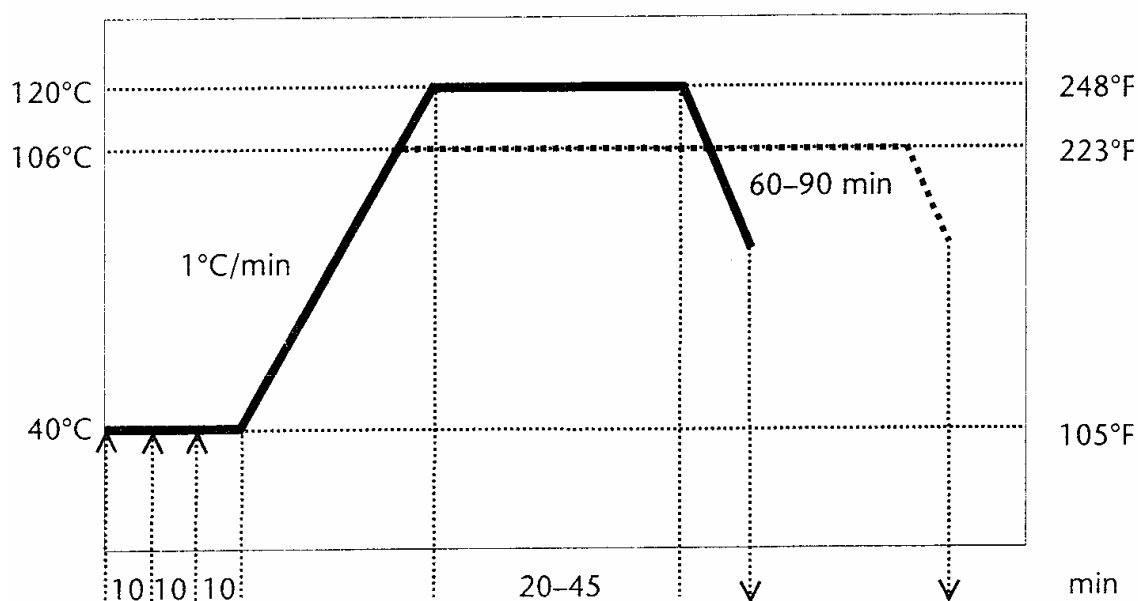
A	0.5 g/l	CIBAFLOW CIR or ALBEGAL FFA
	1 g/l	MIRALAN Q
B	0.5%	ALBEGAL SET
	4%	IRGASOL HTW NEW or MIRALAN HTP
	0-2 g/l	UNIVADINE PB
	1 g/l	Sodium acetate cryst.
	X%	Acetic acid 80%
	pH 4.5	
C	y%	LANASET dyes
	z%	TERASIL dyes.

The pH of the dye bath can be set with 3–5 g/l CIBATEX AB-45 instead of using acetic acid and acetate.

A hydrosuffite reduction clear after dyeing is not recommended owing to the sensitivity of wool to this process. A wash-off with 2 g/l Ciba ERIOPON OS at pH 4–5 at 70°C for 20 minutes is recommended for deep shades to remove disperse dye stains from the wool.

6.2   Dyeing wool/polyamide blends

Wool/polyamide blends can be dyed using a number of dyestuff classes. As wool and nylon are to a degree chemically similar they can by and large be dyed by the same dyestuffs.

Examples of two different dyeing systems, viz. premetallised and reactives, are given below.

a.   Wool/polyamide blends dyed with premetallised dyes

Outlets

Polyamide fibres are often blended with wool to strengthen its mechanical properties without losing the typical wool character. Main outlets for this blend are woollen fabrics for coats, knitting yarns for socks and carpet yarns. The main WO/PA blend ratio is 80/20.

Dyeing system

Polyamide is chemically related to wool because amino groups are integral components of both fibers. Therefore, polyamide can be dyed with the same dyes as wool. The LANASET dyeing system offers the following advantages:

- coverage of a wide range of colours, including brilliant shades

- one-bath dyeing method

- excellent tone-in-tone dyeing of both fibres

- trichromatic systems available

- good light fastness for carpet yarn dyeing

- ideal for deep shades due to high wet fastness.

Parrameters influencing partition between wool and polyamide:

Polyamide fibre type

The most common polyamide types are PA 6 and PA 66. PA 6 has higher dye affinity than PA 66 and, therefore, needs more blocking agent to achieve solid shades on its blends with wool. Beside this difference based on chemical composition, the fibre fineness (dtex), fibre surface/cross section (round, trilobal etc.), degree of delustering, texturing and pretreatment (heat setting) influence the colour depth on polyamide.

Wool fibre

Quality and type, fibre diameter and pretreatment all influence the uptake and shade depth on wool. If the wool has been treated by a shrink-resist-process, its dye affinity is increased appreciably. In most of these cases wool then dyes to a darker shade than the polyamide blended with it.

Blocking agent

Blocking agents like ERIONAL RF or CIBAFIX PAS consist of colourless anionic compounds having high affinity for polyamide. They partially saturate the polyamide fibre and allow the dye to move onto the wool portion of the blend. The amount of blocking agent has to be adjusted so that an even distribution can be achieved between the fibres. The required amount of blocking agent depends on the dyes used, dye concentration, fibre type and blend ratio, and has to be determined in preliminary lab trials simulating bulk conditions as closely as possible.

Dye concentration

The distribution of dyes between the two fibres depends strongly on the applied dye concentration. At pale to medium depths below the saturation limit of polyamide, this fibre is generally coloured deeper than wool. Therefore, dye uptake by polyamide must be retarded with a blocking agent such as ERIONAL RF. In medium to deep shades an even distribution between the fibres is often encountered. In deep shades many dye classes dye the wool darker. In such cases the polyamide has to be covered with dyes having high affinity for polyamide.

Dye selection

Besides the dye selection based on end-use requirements such as wet and light fastness properties, each individual dye has different affinity for wool and polyamide. This means that some dyes dye wool darker and some dye polyamide darker. For dye combinations it is very important that the individual dyes distribute more or less evenly between wool and polyamide and they react similarly to the same amount of blocking agent to give good solidity.
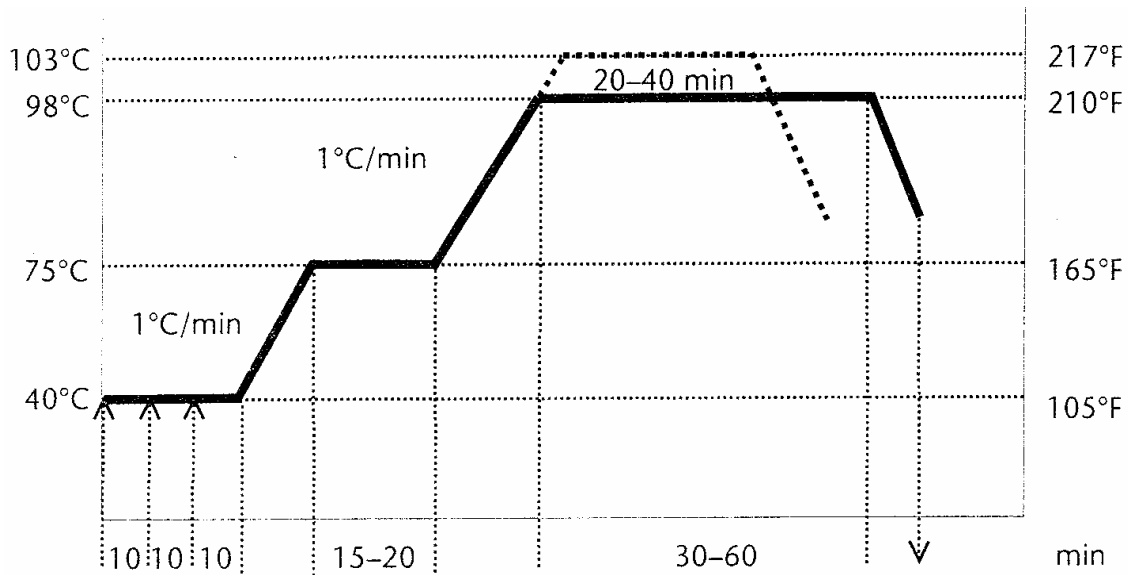
LANASET dye selection

The following table shows the affinity of the LANASET dyes for polyamide. Dyes with low affinity for polyamide need less blocking agent than dyes with medium or high affinity. For combination shades dyes should be selected if possible only from the group with the same affinity in order to achieve best solidity.

The following LANASET dyes are highly suitable for combinations in the more muted shade area, allowing a wide range to be covered:

- LANASET Yellow 2R

- LANASET Red 2GA-01

- LANSET Brown B

- LANASET Grey C

- LANASET Blue 2RA.

Classification of LANASET dyes according to their affinity for polyamide and the necessary amount of blocking agent for good solid shades

Dyeing procedure for WO/PA blends with LANASET dyes

A	0.5 g/l	CIBAFLOW CIR or ALBEGAL FFA
	1 g/l	MIRALAN Q
	0–4 g/l	ERIONAL RF or CIBAFIX PAS
	5%	Glauber's salt anhyd.
	1 g/l	Sodium acetate cryst.
	x%	Acetic acid 80%
	pH 4.5–5.5	
B	1%	ALBEGAL SET
C	y%	LANASET dyes.

* The necessary amount of blocking agent depends on the type of polyamide and the dye concentration used. It has to be determined in preliminary lab trials on the specific material and shade.

Mothproofing of WO/PA blends

MITIN FF is anionic, has affinity for PA and acts like a blocking agent. The blocking effect is very selective and can impair shade solidity. Therefore, an after-treatment at 60–80°C for 30 minutes is recommended.

MITIN AL-01 has no influence on dye distribution and can be applied in the dye bath.

b.   Wool polyamide blends dyed with reactive dyes

Polyamide fibres have far fewer amino groups capable of forming a covalent bond with LANASOL dyes than wool.

In low amounts, LANASOL dyes give darker shades on polyamide than on wool and a suitable amount of ERIONAL RF has to be added to the dye bath to block the polyamide and ensure solidity. With 1–1.5% LANASOL dye and more, the wool dyes to a deeper shade. The depth of dyeing depends on the affinity of the polyamide fibre for the dye (Polyamide 6 has higher affinity than Polyamide 66).

Standard combination:

LANASOL Yellow 4G

Mixture of:

LANASOL Red B (ca. 70 parts)

LANASOL Red 6G (ca. 30 parts)

LANASOL Blue 3G.

For black shades, LANASOL Black PV is recommended.

When wool dyes to deeper shades, the shade of the polyamide component can usually be adjusted to that of the wool with selected LANASET or LANACRON dyes (with an addition of ALBEGAL SET):

Bright shades	Muted shades
LANASET Yellow 4GN	LANASET Yellow 2R
LANASET Red 2B	LANASET Orange RN
LANASET Blue 2R	LANASET Red G
	LANASET Bordeaux B
	LANASET Brown B
	LANASET Grey G
	LANASET Black B
	LANACRON Red S-3G
	LANACRON Red Brown S-R
	LANACRON Navy S-G

6.3   Dyeing wool/acrylic blends

Outlets

The most important outlets for acrylic/wool blends are knitted textiles for sportswear, leisure wear and fashionable men's and women's outerwear, plus hand knitting yarns.

These blends are dyed primarily in yarn form as packages or muffs. Hand knitting yarns and high quality machine knitting yarns are also hank-dyed for the best results.

a.   Dyeing system using premetallised and basic dyes

A suitable dyeing system comprises LANASET/MAXILON dyes, the main benefits of which are:

- coverage of a wide range of colours, including brilliant shades

- trichromatic systems available

- pale to deep shades attainable, including navy and black

- good overall light and wet fastness

- one-bath, two-stage dyeing method except for black

- good stability of the dye bath containing LANASET and MAXILON dyes.

MAXILON dye selection

The most important criteria for selecting cationic dyes are sensitivity to reduction and preservation of the wool.

The trichromatic system for acrylic/wool comprises:

- MAXILON Golden Yellow GL

- MAXILON Red SL

- MAXILON Blue SL.

For green shades and flair control, MAXILON Yellow GL and MAXILON Blue SG are very suitable.

Dyeing procedure for WO/PAN blends with LANASET and MAXILON dyes
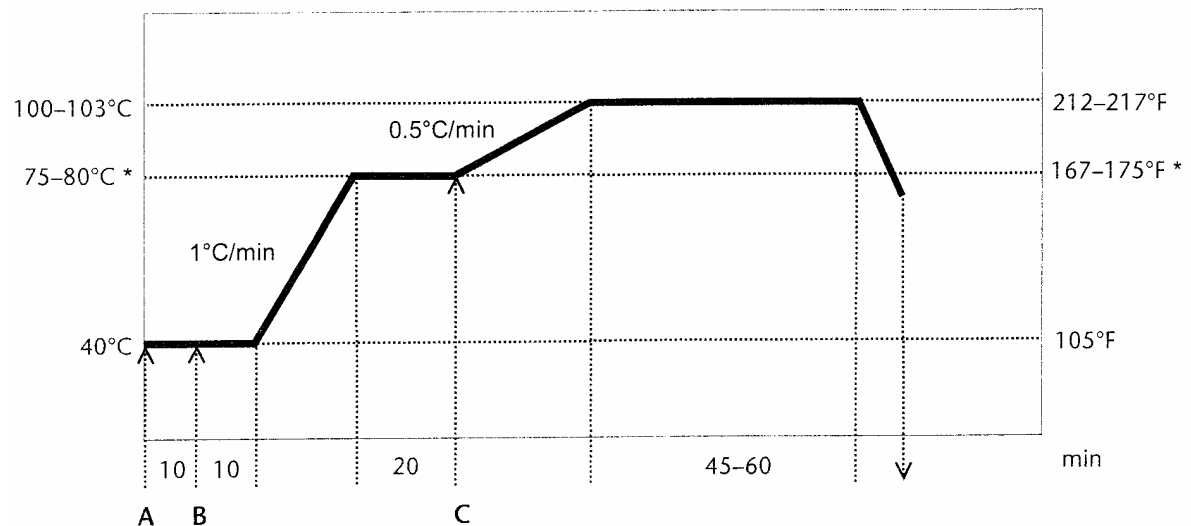
*Below the glass transition point of the PAN fibre used.

A	0.5 g/l	CIBAFLOW CIR or ALBEGAL FFA
	1 g/l	MIRALAN Q
	0.5–1%	ALBEGAL SET
	0–3%	Glauber's salt anhyd.
	1 g/l	Sodium acetate
	x%	Acetic acid 80%
	pH 4.5	
B	y%	LANASET dyes
C	z%	MAXILON dyes
	0–1%	TINEGAL MR NEW.

The pH of the dye bath can be set with 3–5 g/l CIBATEX AB-45 instead of using acetic acid and sodium acetate. The wet fastness of deep shades can be improved by washing off with 1 g/l IRGASOL DAM (pH 4.5) for 20 minutes at 60–65℃ followed by thorough rinsing.

Black shades

Blacks are dyed in a two-bath process, dyeing first the acrylic fibre and subsequently in a fresh bath the wool portion.

## b.   Dyeing system using reactive and basic dyes

A suitable dyeing system comprises LANASOL / MAXILON dyes.

The trichromatic system for acrylic/wool comprises:

* MAXILON Golden Yellow GL

* MAXILON Red SL

* MAXILON Blue SL.

For green shades and flair control, MAXILON Yellow GL and MA XILON Blue 5G are very suitable.

Dyeing procedure for wool/acrylic with LANASOL and MAXILON dyes
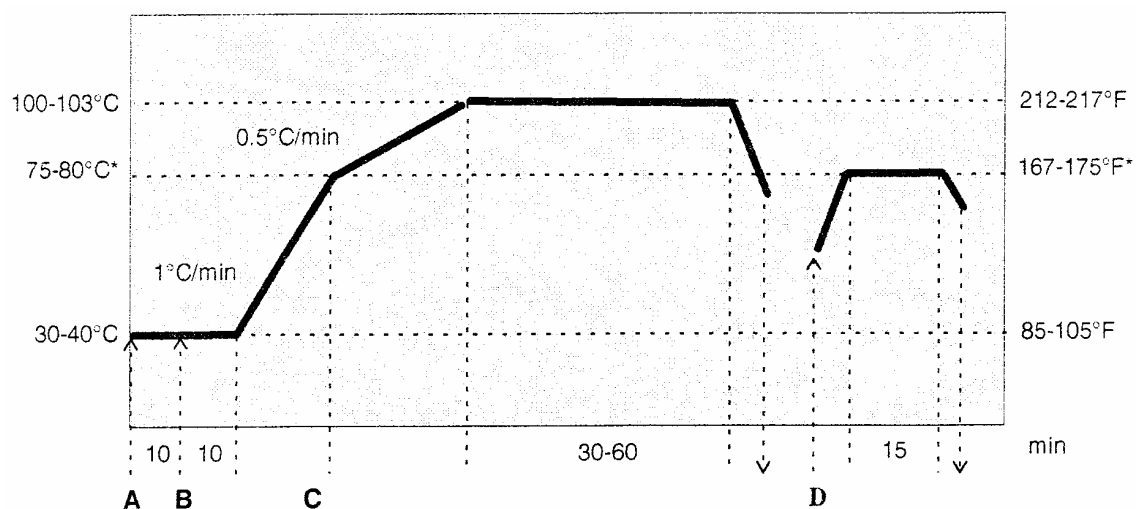
A	0.5 g /1	ALBEGAL FFA
	2–3%	ammonium sulphate
	5%	Glauber's salt anhyd.
	0.5–1%	ALBEGAL A or ALBEGAL SET
	0.5–1%	ALBEGAL B
	x%	Acetic acid 80%
	pH 6.5–4.5 (see pH curve)	
B	y%	LANASOL dyes
C	z%	MAXILON dyes
	0.5–1%	TINEGAL MR new
D		Preferably in a fresh bath at 75–80℃*

-x % ammonia or soda ash *or* sodium bicarbonate pH 8.0–8.5.

Rinse warm and cold, acidify with 1% formic acid 80% in the final rinsing bath.

The wet fastness of deep shades can be improved by washing off with 1g/l IRGASOL DAM (pH 4 with acetic acid) for 20 minutes at 60–65°C followed by thorough rinsing.

* Below the glass transition point of the PAN fibre used.

** If necessary adjust pH to 4-4.5.

6.4   Dyeing wool/silk blends

Outlets

Wool/silk blends are mainly used for apparel in woven or knitted form to give them a luxury character. A large variety of blend ratios can be found ranging from 5 to 50% of silk. WO/S blends are dyed in piece form or as yarn on packages and hanks.

Dyeing system

Silk is chemically related to wool because amino groups are integral components of both fibres. Therefore, silk can be dyed with the same dyes as wool. The LANASET dyeing system offers the following advantages:

- coverage of a wide range of colours, including brilliant shades
- one-bath dyeing method
- excellent solid shades
- trichromatic systems available
- pure silk, pure wool and blended goods can be dyed with the same dyes

Parameters influencing partition between wool and silk

Silk fibre type

The quality and type of silk fibres, for example, mulberry silk, tussah silk, weighted silk, influence the distribution of dyes between silk and wool. The silk used in blends should be

de-gummed before fibre blending to avoid negative influence of the silk gum on dyeing performance and fastness.

Wool fibre

Quality and type of wool, fibre diameter and pretreatment all influence dye uptake and shade depth on the fibre. If the wool has been treated by a shrink-resist-process, the dye affinity is increased appreciably. In most of these cases wool then dyes darker than the silk blended with it.

Amount of salt

Glauber's salt is the major reagent to control the distribution of dyes between wool and silk. Salt retards the dye uptake on wool in favour of silk.

Dyeing temperature

Dyeing at a low temperature favours a deeper dyeing on silk. However, too low a dyeing temperature has a negative influence on wet fastness on wool. The best temperature for LANASET dyes for this blend is 90°C/194°F.
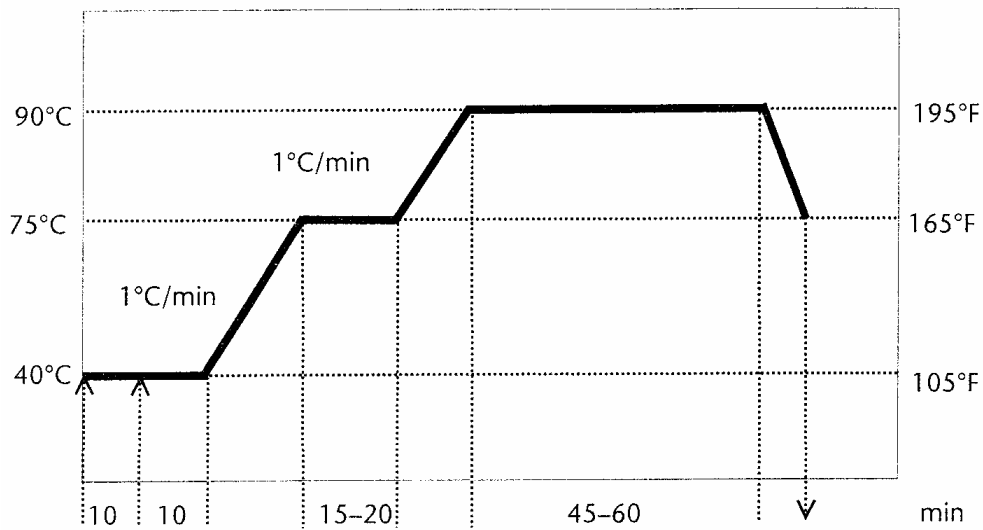
Dyeing pH

The distribution of dyes between the two fibres depends on the pH used. A lower pH favours a deeper dyeing of silk. To obtain reproducible results, the use of a buffer such as sodium acetate is recommended.

LANASET dye selection

With most LANASET dyes solid shades can be achieved on wool/silk blends. Therefore, the normal recommendations, including the trichromatic system LANASET Yellow 2R, Red G and Gray G, can be followed with the following exceptions:

- LANASET Red 2B, Blue 2R, Blue 2RA and Navy R dye silk lighter than the other LANASET dyes. Dyeing at pH 4.5 and using higher amounts of salt can improve the depth on silk.

- Blue shades – Good partition is obtained by a combination of LANASET Blue 5G and Violet B.

- Navy blues – Solid shades can be achieved by a combination of LANASET Navy R and Black B. Alternatively, navy blues could be based on LANACRON Navy S-G 150%.

- Blacks – Dyeings with LANASET Black B need less salt and only 0.5% ALBEGAL SET.

Dyeing procedure with WO/S blends with LANASET dyes

A	0.5 g/l	CIBAFLOW CIR or ALBEGAL FFA
	1 g/l	MIRALAN Q
	1%	ALBEGAL SET
	10–40 g/l	Glauber's salt anhyd.
	1 g/l	Sodium acetate cryst.
	x %	Acetic acid 80%
	pH 4.5–5.5	
B	x %	LANASET dyes

Note: To establish the best dyeing conditions for solid shades, laboratory trials under identical conditions are recommended.

Wet fastness on silk is generally lower than on wool. If necessary, an after-treatment in a fresh bath with 2% CIBAFIX ECO at pH 5–6 for 20 minutes at 40°C/104°F can be given to improve wet fastness.

6.5   Dyeing wool/cotton blends

One-bath dyeing processes for shrink-resistwool/cotton blends

PROCESS DEVELOPMENT BULLETIN No. 45

PURE NEW WOOL

TECHNICAL MARKETING DEPARTMENT

SUMMARY

This bulletin provides information on one-bath dyeing methods for shrink-resistwool/cotton blends. The methods were developed in Australia by Rocklea Spinning Mills for their 30/70 Hercosett wool/cotton yarn, named Colana, in conjunction with CSIRO Textile and Fibre Technology, with the financial support of Australian woolgrowers through The Woolmark Company. The methods are applicable to both yarn and piece dyeing.

For further information contact:

Technical Marketing Department
The Woolmark Company Limited
Valley Drive
Ilkley
West Yorkshire
LS29 8PB
England
Telephone: +44-1943-601555
Facsimile: +44-1943-601521
Contact: P.A. Duffield (Ext. 2565).

6.5.1   INTRODUCTION

Wool/cotton blends have been commercially available for many years but the long and often costly dyeing processes that they required have limited their success in the market place. This has been particularly true for blends of shrink-resistwool with cotton. Such blends are increasingly being used to improve the easy care properties of products, but they create greater challenges for dyers. Fibre dyeing is the simplest technical option, but is often not a commercially viable route. Simple techniques that cause minimum damage to either of the fibre components are therefore required for yarn and piece, dyeing wool/cotton blends.

Dyeing methods are described for three ranges of dyes. Two of the methods are based primarily on reactive dyes and one on a direct/acid system. The dyeing methods described in this bulletin have been used commercially on 'Colana', a 30/70 shrink-resistwool/cotton blend developed by Rocklea Spinning Mills. Modifications may be required for other blend ratios.

Further research on dyeing methods for other dyestuff ranges on shrink-resist wool/cotton blends is currently being conducted by CSIRO Textile and Fibre Technology, Rocklea Spinning Mills and The Woolmark Company.

6.5.2 PREPARATION

The preparation steps for shrink-resist wool/cotton blended products will depend upon the substrate form, the nature of the product (carded or combed cotton) and the machinery available. It may include de-sizing, setting, scouring and/or bleaching. All processes should, where possible, avoid treatment under alkaline conditions. Excessive alkali will cause damage to the wool fibre. Even low levels of alkali will lead to an increase in the affinity of wool for cotton dyes. In some shades this may lead to difficulties in achieving solidity between the two fibres. Additionally, fabric processing should, where possible, be carried out with minimum warp tension, to maintain the aesthetic and technical properties that wool contributes to the blend.

6.5.3 Sizing and de-sizing

The de-sizing process will be determined by the nature of the size applied. On shrink-resist wool/cotton yarns, PVA and acrylic sizes perform very well and are recommended.

However, for economy, products consisting of a combination of starch and synthetic size are often used, since the latter helps to maintain elasticity of the yarn, contributed by the wool fibre. De-sizing processes, therefore, need to remove both the starch and synthetic components.

To remove the starch component, enzyme de-sizing methods are acceptable. When PVA is also present, a high temperature (60–80°C) with a detergent is necessary to remove the product. However, for colour woven fabrics it is important that the temperature is not higher than 60°C to minimise cross staining.

6.5.4 Scouring

To ensure good penetration of the cotton fibre, it is important to remove all waxes and processing oils. The normal alkaline scouring processes for cotton yarn or fabrics must be avoided to minimise damage to the wool fibre and reduce wool staining in dyeing. The following, mildly acid/neutral process has been found to be satisfactory:

Set the bath with:

- scouring, agent   2.0-3.0 g/l

- de-aerating agent 0.25 g/l (for yarn scouring)

- sequestering agent   0.5 g/l.

Ensure pH is in the range 6–8.

Raise to 90°C and run 30 minutes.

Drain hot (at or above 80°C) to minimise re-deposition of cotton wax.

Rinse hot, 10 minutes.

Rinse warm, 10 minutes.

Rinse cold, 10 minutes.

Appropriate scouring agents must be used. Felosan RGNS (CHT) and Croscolor SDCF (Crosfield) have proved to be successful. Ultravon GP-N is recommended by Ciba. Verolan NBO (Rudolf) has been used successfully as a dispersant/sequesterant. Irgalon PS is the Ciba recommended sequestering agent. Alternative products from other suppliers may be equally suitable, but should be evaluated before use.

6.5.5 Pre-bleaching

Conventional cotton pre-bleaching methods can cause excessive damage to wool and, therefore, alternative processes must be used.

Neutral or mildly acid bleaching processes have yet to be fully evaluated commercially on shrink-resist wool/cotton blends. However, they are preferable to alkaline methods to reduce wool staining in subsequent dyeing.

The following may be used:

- prestogen W (BASF)   2–5 g/l

- hydrogen peroxide (35 %)   10–25 ml/l

- wetting agent   0.5 g/l.

Raise to 75°C, run 30–45 minutes.

Rinse well.

Note that pre-bleaching may increase the level of wool staining in subsequent dyeing.

A separate publication will be produced describing, methods of bleaching and fluorescent whitening of shrink-resist wool/cotton blends.

6.5.6 Dyeing

Anionic retarders (reserving agents)

Shrink-resist wool has a greater affinity than untreated wool for anionic dyes. The use of an anionic retarder is therefore necessary to control dye uptake. Typical application levels can be up to 6% on total weight of goods depending on the shade.

Note: For an anionic retarder to be of benefit, it must be added to the dye bath before any dyes.

Examples of suitable products are Cibatex RN (Ciba), Dyapol WX (Yorkshire), Nylofixan P/PM and Thiotan HW (Clariant). Other products may be equally suitable but have not yet been evaluated.

a.   Cibacron LS method (patent pending)

Cibacron LS dyes

Cibacron LS (Ciba) dyes are most suitable for heavy shades on shrink-resist wool/cotton blends. These dyes will dye the cotton and, to some degree, the wool portions of the blend. The affinity of cotton reactive dyes for shrink-resist wool is much greater than for untreated wool. For this reason, modified dyeing conditions and auxiliary concentrations are necessary when dyeing shrink-resist wool/cotton blends. Lanasol dyes must be included, where appropriate, to fill in the shade on the wool component. Some of the Cibacron LS dyes perform better on shrink-resist wool/cotton blends than others with respect to dyeing properties and fastness performance. Industrial trials have shown that these dyes are very liquor ratio sensitive (that is, their wool staining propensity changes with differing liquor ratios). This factor makes them more suited to package dyeing where liquor ratios can be carefully controlled.

The recommended trichromat is:

- Cibacron Yellow LS-R

- Cibacron Orange LS-BR

- Cibacron Blue LS-3R.

This combination gives the best performance, in terms of light fastness and partition. For red shades that cannot be matched with this combination, Cibacron Red LS-B may be used, or for scarlet shades Cibacron Scarlet LS-2G.

Cibacron Navy LS-G	Suitable for navy and black shades, that is, at 2% depth or greater.
Cibacron Brilliant Blue LS-G	Suitable for bright blue and royal shades.

Also:

Cibacron Yellow LS-4G	For green and blue/green shades.
Cibacron Black LS-N	Suitable for blacks at depths > 8%.

Cibacron Green LS-G should **not** be used, since its shade is altered by reduction in the presence of wool.

Wool dyes

Of the classes of wool dyes available, only reactives are suitable for co-application with Cibacron LS dyes on shrink-resistwool/cotton. The Ciba wool reactive dye range is Lanasol and the recommended trichomatic dyes are:

- Lanasol Yellow 4G

- Lanasol Red 6G

- Lanasol Blue 3G.

Supplementary dyes in the range may be used, according to the shade being matched. In recipes that contain Cibacron Orange LS-BR or Cibacron Red LS-B, it may be possible to omit, or minimise Lanasol Red 6G, since the Cibacron dye will also dye the wool component.

Black and navy shades should be based on Lanasol Navy MBN (Lanasol Navy B and Black R are unsuitable for this method).

The basic dyeing process is illustrated below:

Shrink-resistwool/cotton dyeing method with Cibacron LS and Lanasol dyes

A	De-aerating agent	0.5 g/l
	Sequestering agent	0.5 g/l
	Anti-reduction agent	1.0 g/l
	Anionic retarder (Cibatex RN)	2–5%
	Dispersant/protective colloid (optional)	2.0 g/l
	Salt*	10–50 g/l
	Acetic acid/soda ash to pH 7.0	(including navy and black)

B Dyes

C Soda ash 5–10 g/l (dosed or added in portions over 15–30 minutes) to ensure a final pH of 9.8–10.2 (anionic retarders have a buffering effect and consequently more soda ash is required as retarder levels increase).

Cibacron Dye (%)	Salt Concentration* (g/l) LR 10:1
0 - 0.5	10
0.5 - 1.5	15
1.5 - 2.5	20
2.5 -	30
Black/Dark Navy	50

*Common salt or Glauber's (anhydrous) salt may be used.

Washing-off

Rinse cold to remove excess dye, salt and alkali.

Before washing off hot, the bath must be neutralised to pH 7.0 at 40–5O°C, with acetic acid to avoid damage to the wool component during soaping.

After neutralising, it is beneficial to rinse at 70°C to remove as much hydrolysed dye as possible before soaping, minimising the possibility of further wool staining at elevated temperatures.

Soaping

Set bath with:

- Cibapon R 1 g/l Acetic acid to pH 7–8.

Raise to 90°C and run 10 minutes.

Rinse at 70°C.

For heavy shades the soaping and rinsing should be repeated.

Cationic after-treatment

The wet fastness of heavy shades may be improved by after-treatment with a cationic fixing agent. The application bath should be neutral or slightly acid.

Add 2–3% Tinofix FRD (Ciba) and run 20 minutes at 40°C Hydroextract and dry without rinsing.

Softeners may be applied in the after-treatment bath, providing they are nonionic or cationic.

b.   Kayacelon React method

Kayacelon React (Nippon Kayaku) neutral reactive dyes have proved useful in selected shades on shrink-resist wool/cotton blends. They have been found to be unaffected by variations in liquor ratio and this makes them ideal for both yarn and piece dyeing. Their major application is in dyeing very pale to medium shades and for turquoise blues and bright greens. They dye cotton and to some degree also the wool component. For this reason, small quantities of wool dyes can be added to achieve a solid shade on both fibres. Lanasol dyes are suitable for this purpose.

Preparation

Neutral scouring is recommended. The same pre-bleaching process may also be used.

Dyeing process

The dyeing process for Kayacelon React and wool dyes is shown below. A temperature hold at 75°C assists levelness and is essential for pale shades and dyeing machines with less than optimum liquor circulation.

Shrink-resist wool/cotton dyeing method with Kayacelon React and wool dyes
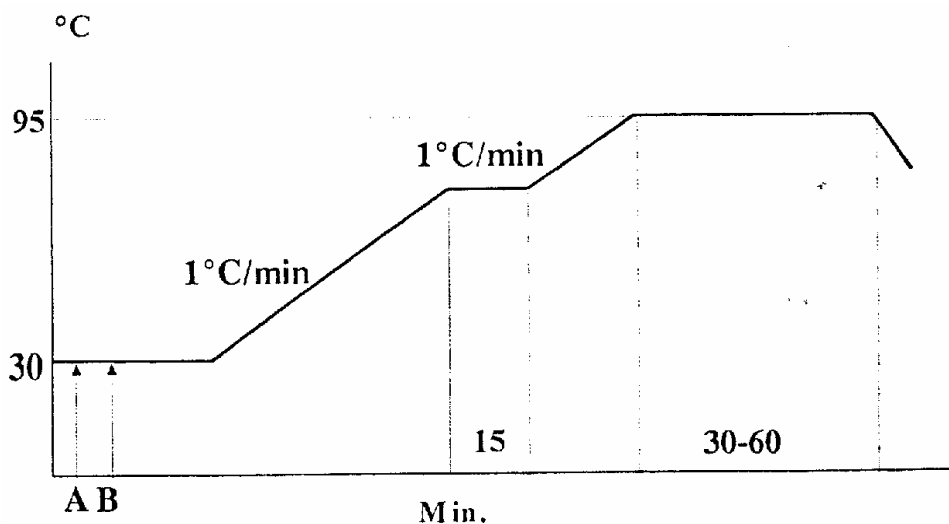
A	Salt*	20–80 g/l
	Sequestering agent	0.5 g/l
	Dye bath lubricant	1.0 g/l
	Anti-reduction agent	1.0 g/l
	Anionic retarding agent	0–2%
	Buffer to	pH 7.0
	Or use:	
	Kayaslide 608	1–2 g/l
B	Dyes (added slowly at 30°C)	

Kayacelon React Dye	Salt Concentration*
<0.1%	20g/l
0.1-0.3%	30g/l
0.3-1.0%	40g/l
1.0-2.5%	60g/l
>2.5%	80g/l

*Common or Glauber's (anhydrous) salt may be used.

Kayacclon React dyes are selected on the basis of low or minimal wool staining. The following dyes have proved suitable:

- Kayacelon React Yellow CN-ML (main trichromat yellow)

- Kayacelon React Red CN-3B (main trichromatic red)

- KayacelonReactBlueCN-MG (maintrichromatblue).

In this trichromatic combination the blue shows the most staining of shrink-resist wool, thus wool normally has to be shaded with red/yellow wool dyes.

For turquoise shades, Kayacelon Turquoise CN-2G has proved an excellent choice.

For emerald greens, the above turquoise in combination with Kayacelon React Yellow CN4G is a suitable combination.

Kayacelon React Dark Blue CN-R can be used for dark blues. This dye exhibits minimal wool staining and the wool must be filled in with appropriate wool dyes accordingly (in contrast to the Blue CN-MG, which stains wool more heavily).

After dyeing the material should be cooled, rinsed warm and drained. Soaping may be carried out at 80–90°C, as required.

Cationic fixation of dyes and softening may be carried out as describe above for Cibacron LS dyes (section 3.2.5

c.   Indosol SF/Optisal method

Direct dyes have proved useful for selected shades on shrink-resist wool/cotton blends. Their main application is for pale shades requiring no after-treatment on yarn packages and shades up to heavier depths on piece goods, where the after-treatment is more easily applied. Many ranges of direct dyes are available, of which some may be suitable for shrink-resist wool/cotton blends. At present only Indosol SF and Optisal dyes (Clariant) have been evaluated on this substrate. Indosol SF and Optisal dyes that show low wool staining must be selected for dyeing shrink-resist wool/cotton blends. A cationic after-treatment is essential to achieve adequate wet fastness on all except pale shades.

Preparation

Neutral scouring is recommended. The same pre-bleaching process may also be used.

Dye selection

The following dyes have partition properties that lead to acceptable levels of wool staining when applied to shrink-resist wool/cotton blends:

- Indosol Yellow SF-GL 160

- Indosol Yellow SF-2RL

- Indosol Brown SF-BR

- Indosol Br. Red SF-R

- Indosol Rubinole SF-RGN

- Indosol Blue SF-GL ')70

- Indosol Blue SF-2G 400

- Indosol Navy Blue SF-BL 240

- Indosol Navy Blue SF-BL 240

- Indosol Navy Blue SF-GLE

- Indosol Grey SF-BL 200

- Indosol Black SF-RL

- Indosol Black SF-BLN

- Optisal Red R

- Optisal Red 7B

- Optisal Royal Blue 3PL

- Optisal Dark Blue GL.

A suitable trichromatic combination is:

- Indosol Yellow SF-GL 160

- Indosol Rubinole SF-RGN

- Indosol Grey SF-BL 200.

Dyeing process

The following process may be adapted according to the selection of wool dyes, 1:2 metal complex, milling or reactive.

Shrink-resist wool/cotton dyeing method with Indosol SF/Optisal and wool dyes
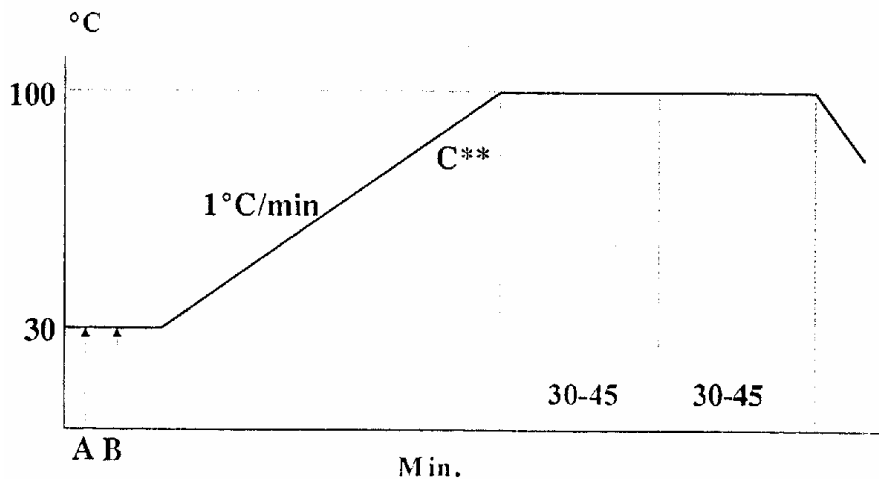
A	Dye bath lubricant	1.0 g/l
	Levelling agent*	
	Amonium sulphate	4%
	Anionic retarder (Thiotan HW)	4–6%
	Acetic acid to	pH 6.5–6.8
B	Dyes	

Glauber's salt additions should be as recommended for 100% cotton.

Notes:

* Levelling agents for wool are not required and may adversely affect dye partition. If a levelling agent is required for the cotton component, Humectol C (Clariant) at between 0.5–1.0% can be used. It is also effective as a dye bath lubricant.

** Common salt or Glauber's (anhydrous) salt may be used.

Cationic after-treatment

A cationic after-treatment is essential to achieve good wet fastness on all except pale shades. The following process is recommended for use with Indosol dyes:

Set the bath cold with:

Sodium sulphate   5 g/l

Indosol E50 Liquid   0.5-2.0%

Ammonia/acetic acid to pH 6.5-7.0.

Raise to 6°C; run 15–20 minutes.

Rinse cold.

For recipes containing only Optisal dyes the following procedure is recommended:

Set bath at 4°C with:

1–4% of Optifix F liquid or Solfix E liquid.

Run for 10 minutes and slowly add:

Soduim carbonate 3 g/l.

Run for 10 minutes.

Drain, rinse, neutralise cold with acetic or formic acid for 10 minutes.

Rinse cold.

Summary

The recommended dyeing procedures and processing routes for the various shade areas are given in the following table. It is recommended that in all instances preliminary trials are carried out.

Recommended dyeing procedures

Dyeing procedure	Processing route	Shade area
Cibacron LS	Yarn dyeing	Medium–Heavy
Kayacelon React	Yarn and piece dyeing	Pale–Medium
Indosol/Optisal	Piece dyeing	Medium–Heavy

Machinery

a.   Package dyeing

Shrink-resist wool/cotton yarn may be dyed as muffs or as soft wound packages to maximise bulk for knitwear, or on conventional packages for woven products. Further information on package dyeing may be found in *Woolmark Process Development Bulletin No. 22*.

b.   Piece dyeing

It is recommended that the dyeing of shrink-resist wool/cotton fabric be carried out only using Overflow/Softflow jet dyeing machinery. These machines have excellent pumped liquor circulation, which is essential if level dyeing of the wool component is to be achieved. In addition, the good liquor/fabric interchange assists in the removal of unfixed dyes and auxiliaries during soaping and rinsing.

Colour fastness requirements

The colour fastness of non-washable and washable, shrink-resist wool/cotton products that carry a Woolmark Blend label, that is, with a wool content of 50% or greater, should meet the Woolmark Colour Fastness Specifications. These are given in Appendix 2. Products that do not carry a Woolmark Blend label should meet customer specifications, as appropriate. However, if they are to carry a Colana label, they should also meet Rocklea specifications for that product. Details are also given in Appendix 2.

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7.   Preserving the quality of wool

Because of the chemical and physical nature of the wool fibre it may be damaged considerably by any number of dyeing and finishing processes. For example, dyeing wool at very low or very high pH and at elevated temperatures may cause damage to the fibre that will result in difficulties during later processing and reduced quality of the finished items.

Also, normal dyeing procedures impart a high degree of 'permanent set' to the wool fibre and this permanent set may lead to problems during later processing.

There are a number of options available to the dyer for minimising the amount of damage done to the wool fibre during dyeing and some of these will be examined below.

7.1   Low temperature dyeing

7.1.1   The Sirolan-LTD wool dyeing process

Improved product quality with economic benefits and cleaner effluent

J.A. Rippon, F.J. Harrigan, A.R. Tilsonl #
CSIRO Division of Wool Technology
Geelong Laboratoy, Belmont, Victoria, Australia

ICI Valchem, Ascot Vale, Victoria, Australia

Synopsis

Fundamental studies at the CSIRO Division of Wool Technology on the diffusion of dyes into wool [1, 2] have led to the development of a new approach to wool dyeing, called the Sirolan-LTD Process [3, 4]. In this method, the cell membrane complex of wool is modified before dyeing by treatment under mildly alkaline conditions with a special auxiliary (Valsol LTA-N), jointly developed by CSIRO and ICI Australia. Wool pretreated with Valsol LTA-N has an increased rate of dye bath exhaustion and dye penetration early in the dyeing cycle. This enables the treated material to be dyed in one of two ways; either at a temperature below the boil for a similar time to the conventional cycle, or for a shorter time at the boil compared with the conventional cycle. The low temperature and short-time-at-the-boil dyeing procedures can be used with all wool dyestuff classes, in all depths of shade. The methods are suitable for untreated and shrinkresist-treated wools and wool/nylon blends. In addition to good macro-levelness and excellent coverage of tippiness, the low temperature and short-time-at-the-boil versions of the Sirolan-LTD Process give higher exhaustion levels of dyestuffs and insect-resist agents and hence cleaner effluent liquors, compared with other dyeing methods. Fastness properties are comparable with those from conventional dyeing procedures at the boil. Both methods cause significantly less fibre damage than other wool dyeing procedures. The reduction in damage is reflected in improved processing performance of the dyed wool. The Sirolan-LTD method for dyeing wool at sub-boil temperatures and the short-time-at-the-boil version of the process are in commercial use in Australasia and are currently being introduced into Asian and European dye houses.

Introduction

Conventional methods used in wool dyeing involve prolonged periods at, or near the boil; this is necessary in order to obtain good levelling and also penetration of dyes into the fibre. Conventional dyeing methods can cause modification, or 'damage', to the fibre, which often results in unacceptable levels of yellowing and an impairment of performance during wear. Furthermore, when wool is dyed early in the processing sequence, production rates

and yields in operations such as carding, spinning and weaving are usually lower than for undyed material [3, 4].

The amount of fibre damage that occurs when wool is dyed depends on the dye bath pH and the time/temperature profile of the dyeing cycle [2]. Wool is composed of polypeptide chains held together by several types of chemical and physical bonds, which stabilise the structure of the fibre [2]. The most important of these are the (covalent) disulphide cross-links, which act as bridges between different polypeptide chains, and also the electrostatic interactions between acidic and basic groups present in the side chains of some of the amino acids.

These 'salt linkages' are important in wool dyeing because their concentration in the fibre changes with pH. Depending on the dyes and equipment used, wool dyeing is carried out at a pH in the range pH 2–7. When wool is boiled in an acidic dye liquor damage occurs to the protein structure mainly by hydrolysis of the peptide bonds [2]. In some circumstances setting of fibres into new configurations may also contribute to a reduction in fibre strength [5]. In conventional dyeing cycles at the boil, the level of fibre damage can be minimised to some extent by maintaining the dye bath pH at a value around the iso-electric region of wool (pH 4–5). Under these conditions the concentration of charged amino and carboxyl groups is at a maximum and, hence, their stabilising effect on the wool proteins is greatest. Several ranges of dyes are now available that are suitable for application around pH 4–5. In addition to dyeing at pH values within the iso-electric region, fibre damage can be further decreased by dyeing at temperatures below the boil, or by shortening the time at the boil. The beneficial effects on wool quality of lowering the dyeing temperature or decreasing the dyeing time have been known for many years. However, attempts to introduce dyeing procedures based on either of these approaches have met with only limited success because of problems with dye penetration and poor fastness properties in heavy shades.

A new approach to wool dyeing

Fundamental studies by the CSIRO Division of Wool Technology, on the diffusion of dyes into wool, have shown that dyes penetrate the fibres at the junctions between cuticle cells (scales) [1, 2]. The nonkeratinous regions of the fibre, in particular the cell membrane complex, were also shown to be important pathways for dye diffusion in the early stages of a dyeing cycle. It has been suggested that lipid material at cuticular junctions [6] and inside the fibre [7] impedes dye penetration. The presence of nonkeratinous proteins in the cell membrane complex has also been implicated in retarding the diffusion of dyes into wool [8].

The CSIRO investigations led to the development of the Sirolan-LTD process for dyeing wool at temperatures below the boil [3]. The key to this dyeing method was a special auxiliary, used to treat the wool under mildly alkaline conditions before dyeing. The pretreatment modified the nonkeratinous regions at the scale edges and inside the fibre. Small amounts of lipid and nonkeratinous proteins were removed and there was some uptake of the reagent by the substrate. The treated material had improved dyeing properties, showing increased rates of dye exhaustion and diffusion into the fibre. This enabled the pretreated wool to be dyed to a satisfactory standard at 85–90°C instead of at the boil. The auxiliary used in the earlier work gave optimum results only when used in a two-bath procedure [3]. In this method, the pretreatment liquor was discarded, the machine re-filled and the wool dyed from a fresh bath set to the required pH, but without addition of conventional levelling agents. It was necessary to dye the pretreated wool from a fresh liquor because the presence in the dye bath of the original version of the auxiliary caused some undesirable effects; namely retardation of dye bath exhaustion and dye desorption (drainage effects) with some premetallised dyes. Joint work by CSIRO and ICI Valchem, carried out since the earlier publication has resulted in the development of a variant of the special auxiliary with a modified structure (now called Valsol LTA-N).

With the development of this version of the auxiliary the disadvantages associated with the earlier chemical have been overcome. This enables the Sirolan-LTD process to be operated as a single-bath procedure, in which the pretreatment and dyeing steps are carried out from the same liquor. The two-bath procedure can still be used with Valsol LTA-N; it may be preferred in some cases; for example, as a substitute for a mild scour where this is carried out prior to dyeing, or where fabrics are scoured and dyed in different machines. In the latter case, the pretreatment can be carried out after the normal scouring procedure. After treatment with Valsol LTA-N, the wool may be rinsed before dyeing, but this is not essential. Rinsing does not affect the enhanced dyeing properties produced by Valsol LTA-N. An interesting and novel feature of this process is that the pretreated wool may be rinsed, dried and stored until required for dyeing. It has been shown that the improvement in dyeing behaviour of the treated material is retained even after storage for more than one year.

Since its introduction for low temperature dyeing, Valsol LTA-N has been found to be an excellent levelling agent for dyeing at the boil. The increased rate of dye bath exhaustion and fibre penetration produced by treatment with Valsol LTA-N, coupled with its superior dye levelling properties, enables excellent results to be obtained by dyeing the treated wool at the boil for a much shorter time than in conventional methods. This paper will describe the low temperature and short-time-at-the-boil versions of the Sirolan-LTD process. Only the one-bath application will be discussed, because of its greater use by industry.

The Sirolan-LTD process

Figure 1 shows the steps involved in the low temperature and short-time-at-the-boil versions of the Sirolan-LTD process.
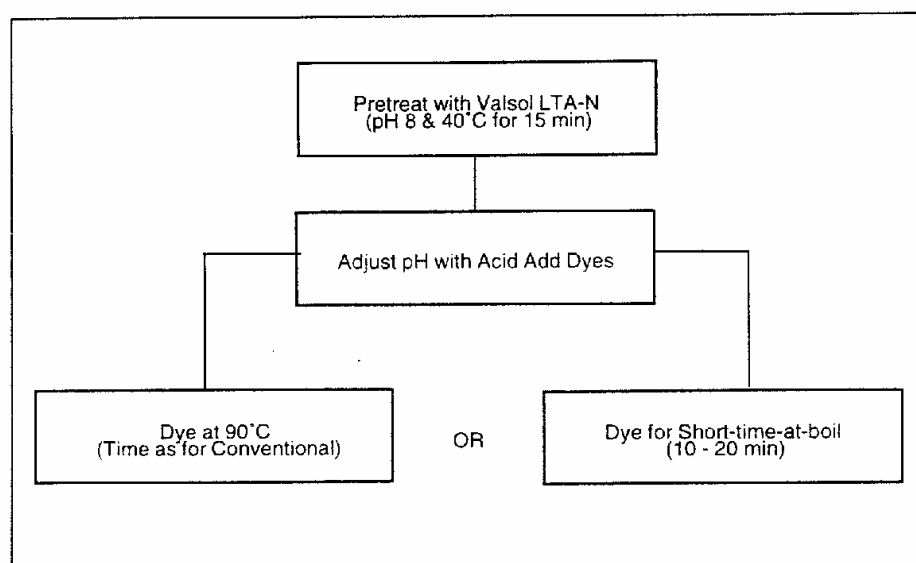
Fig. 1 - The Sirolan-LTD Dyeing Procedure.

The wool is first treated with Valsol LTA-N under mildly alkaline conditions at pH 8.0.

Industrial experience has shown that ammonium hydroxide provides a convenient means of setting the pretreatment pH, but other alkalis such as sodium carbonate or bicarbonate can also be used. The concentration of Valsol LTA-N required depends on depth of shade and liquor ratio. For non-shrinkresist wools, a concentration of the auxiliary in the range 0.5–1.5% oww is recommended for the application of acid levelling, acid milling, 2:1 premetallised, chrome and reactive dyes. When applying 1:1 premetallised dyes (both conventional and Neolan P types), a concentration of 3% oww Valsol LTA-N should be used, in order to ensure good coverage of tippiness on all substrates. A higher concentration of Valsol LTA-N (1.5–2.5% oww) is also recommended when dyeing chlorine/Hercosett or

chlorinated substrates. A treatment time of 15–20 minutes at 40°C is usually sufficient for all application levels. After the pretreatment, the liquor is adjusted with formic acid to pH 5–5.5 for pale shades and pH 4.5 for other shades, up to and including heavy depths. Insect-resist agent (if required) is added at this stage, followed by dyestuffs. Valsol LTA-N has excellent dye levelling properties, both at low temperature and at the boil. Conventional levelling agents should not, therefore, be added to the dye bath; these are unnecessary to obtain good coverage of tippiness and usually reduce the exhaustion levels of dyestuffs and insect-resist agents. Furthermore, with most dyestuff types, even dyeings with good coverage of tippiness can be obtained without addition of sodium sulphate. In a small number of cases, however, sodium sulphate may be necessary to improve fibre coverage with dyes that show skittery dyeing behaviour on some substrates; for example, some reactive dyes in pale shades. In these cases, however, the concentration of sodium sulphate can usually be decreased to around 50% of that used in the conventional method. The only exception to this general recommendation on the use of sodium sulphate is for 1:1 premetallised dyes (conventional and Neolan P types). Fibre coverage is improved with these dyes by adding the amount of sodium sulphate used in the conventional method (8–10% oww).

Fig. 2 - Conventional and Sirolan-LTD dyeing cycles.

Modification of wool by treatment with Valsol LTA-N increases the rate of dye bath exhaustion and rate of dye diffusion into the fibre, early in the dyeing cycle [3.4]. This enables the treated material to be dyed under milder conditions than used in conventional methods. As shown in Figure 1, the pretreated wool can be dyed either at a lower temperature for a similar time to the conventional procedure, or at the boil for a much shorter time. Typical dyeing cycles for the Sirolan-LTD low temperature and short-time-at-the-boil methods are compared with a conventional cycle in Figure 2.

Wool that has been pretreated with Valsol LTA-N can be dyed with all the dyestuff classes used on wool. Both methods are suitable for loose stock, tops, yarn (package and hank) and fabric. They can be used on untreated, chlorinated and chlorine/Hercosett-treated wools and also wool/nylon blends. In the latter case, treatment with Valsol LTA-N improves dyestuff partition between the wool and nylon, in favour of the wool component. This enables the concentration of nylon blocking agent to be decreased to around 50–60% of that normally used, thus giving both cost and environmental benefits.

Benefits observed in the dye house

The following benefits have been found for the Sirolan-LTD low temperature and short-time-at-the-boil dyeing methods.

Coverage of tippiness

The modified scour improves the evenness of dye uptake along wool fibres, because of a lower propensity for preferential dye sorption by damaged parts of the fibre [2, 4]. This effect enables conventional levelling agents to be omitted from the dye bath, as discussed above. An important practical consequence of the effect of treatment with Valsol LTA-N on the dyeing properties of the fibre is a reduction in affinity differences caused by differential weathering of fibre tips and roots [2]. In many cases, coverage of tippiness on the pretreated fibre has been found to be superior to the coverage on untreated wool obtained with conventional levelling agents at the boil.

Exhaustion of dyes and insect-resist agents

High dye bath exhaustion is usually obtained by the Sirolan-LTD methods. In most cases exhaustion levels are better than those obtained by dyeing at the boil with conventional dye-levelling auxiliaries, because the latter often suppress dyestuff exhaustion. Conventional, surfactant-type levelling agents also reduce the exhaustion of permethrin (a synthetic pyrethroid, insect-resist agent), when this is applied to wool during dyeing. Industrial experience has shown that Valsol LTA-N gives excellent dye coverage on weathered wools without suppressing the exhaustion of permethrin [9]. The high exhaustion levels of dyestuffs and insect-resist agents, together with the omission or decreased concentration of sodium sulphate in the dye bath discussed above, result in a reduced effluent load from the dye house.

Fastness properties

Extensive tests covering all types of wool dyestuff classes have shown that both the low temperature and short-time-at-the-boil versions of the Sirolan-LTD process give fastness properties that are comparable with those obtained by conventional methods at the boil. Table I shows alkaline perspiration and rubbing fastness data for some commonly-used premetallised dyes, at various depths.

Table I - Fastness properties of wool dyed by conventional and Sirolan-LTD low temperature and short-time-at-the-boil methods.

Dye	Method	Alkaline perspiration (IWS TM 1 74)			Rubbing (IWS TM 165)	
		Wool	Nylon	Cotton	Dry	Wet
Lanaset Yellow 2R						
(1% oww)	Conventional	4–5	3–4	4–5	4–5	3–4
	Low Temp.	4–5	4	4–5	4–5	3–4
	Short Boil	4–5	3–4	4	4–5	3–4
Lanaset Red G						
(1% oww)	Conventional	4–5	4–5	4–5	4–5	3–4
	Low Temp.	4–5	4–5	4–5	4–5	3–4
	Short Boil	4–5	4	4	4–5	3–4
Lanaset Blue 2R						
(1% oww)	Conventional	4–5	4	4–5	4–5	4
	Low Temp.	4–5	4–5	4–5	4–5	3–4
	Short Boil	4–5	4	4–5	4–5	3–4
Lanaset Grey G						
(1% oww)	Conventional	4–5	4–5	4–5	4–5	3–4
	Low Temp.	4–5	4–5	4–5	4–5	3–4
	Short Boil	4–5	4–5	4–5	4	3–4
Acidol Dark Blue						
M-TR*	Conventional	4–5	4	4–5	4	3–4
(3% oww)	Low Temp.	4	4	4–5	4	3
	Short Boil	4–5	4	4–5	4	3 - 4
Acidol Black						
M-SRL*	Conventional	4–5	4	4–5	4	3
(4% oww)	Low Temp.	4–5	4–5	4–5	4	3
	Short Boil	4–5	4–5	4–5	4	3

Conventional dyed for 40 minutes at 100°C.
Low temperature dyed by Sirolan-LTD method for 40 minutes at 9°C.
Short boil dyed by Sirolan-LTD method for20 minutes at 100°C.

Dark Blue M-TR and Black M-SRL dyed for 60 minutes by conventional and low temperature methods and for 30 minutes by short boil method.
Fastness properties were assessed on SDC Multifibre Test Fabric. Staining was measured on a Datacolor Texflash, according to ISO Grey Scale 105 - A02.

Dyeing at low temperature

In the low temperature version of the Sirolan-LTD process, the dye bath is heated to a dyeing temperature in the range 85–90°C, depending on the dyestuff class and depth of shade. As indicated in Figure 1, the time at the equilibrium temperature should be similar to the time recommended at the boil for the conventional method. In many cases, complete dye bath exhaustion can be obtained at temperatures below 70°C, because of the accelerated rate of exhaustion of dyes onto the treated wool. Furthermore, light micrographs of fibre sections have shown that, for a given dyeing time at temperatures in the range 40–70°C, the degree of penetration of dye into the fibre is increased by the pretreatment. Optimum colour yields and fastness properties are not achieved, however, unless an equilibrium dyeing temperature of 85–90°C is used. The actual temperature required depends on the dyestuff class and the depth of shade. Dye bath equilibrium temperatures of 85–90°C are necessary in order to ensure that the dyes migrate from the lightly cross-linked regions between the cells of the cortex into the high sulphur regions inside the cortical cells. It is important to note that, as in conventional dyeing, if dye remains largely in the nonkeratinous regions rapid diffusion out of the fibre can occur, thus giving rise to poor wetfastness properties [2]. However, as shown by the data in Table I, provided the recommended dyeing conditions are user, the fastness properties of wool dyed by the Sirolan-LTD method at 90°C are comparable with those from conventional procedures at the boil. Figure 2 shows that the overall dyeing times for the low temperature and conventional methods are similar.

Processing performance of wool dyed at low temperature

Industrial experience has shown that wool dyed at low temperature by the Sirolan-LTD Process has a softer handle and significantly better processing characteristics than wool dyed for similar times at the boil. Some of the improvements in processing performance, found from monitoring extensive mill trials, are summarised in Table II.

Table 11 - Effect on processing performance of tops and loose stock of dyeing by the Sirolan-LTD low temperature method.

	% Improvement compared with wool dyed at the boil		
	Worsted (a)	**Woollen (b)**	**Semi-worsted (b)**
End-breaks/1000 spindle hours	25 (c)	86 (d)	81 (e)
Yarn tenacity	4	13	12
Yarn elongation at break	17	14	12
Overall yield	(f)	6	2
Weaving efficiency	10	(f)	(f)

(a)   Top dyed.
(b)   Loose stock dyed.
(c)   38 tex Sirospun yarn spun at 13.5 m/min and 8500 rpm.
(d)   150 tex yarn spun at 28.8 m/min and 6800 rpm.
(e)   350 tex yarn spun at 35 m/min and 4830 rpm.
(f)   Not measured.

These and other data have been described in detail elsewhere. Loose stock dyed at 90°C is less compacted than material dyed at the boil, because the lower dyeing temperature produces a lower degree of set when the wool is in a compressed state. This results in easier opening of the dyed fibre and more efficient drying, thus producing savings in energy. Worsted tops dyed at 90°C have been observed to be bulkier and softer than similar tops dyed at the boil. Dyeing at sub-boil temperatures causes less yellowing of the substrate, which can result in brighter shades.

Benefits in processing have also been found for yarn package-dyed at low temperature. Table III compares yarn properties and weaving performance data of a 64/2 Nm yarn dyed for 60 minutes at 90°C with those of a similar yarn dyed by the conventional method for 40 minutes at 104°C. The yarn dyed by the Sirolan-LTD method at 90°C had better strength, elongation at break and weaving performance than the material dyed by the normal procedure. The fastness properties of the shade (4.6% oww total dyestuff) were similar by the two methods.

Table III - Yarn properties and weaving performance of 6412 Nm yarn dyed by conventional and Sirolan-LTD (low temperature) methods.

	Dyed by conventional method (40 min at 104°C)	**Dyed by Sirolan-LTD method (60 min at 90°C)**
Yarn strength (cN)	217.1	232.4
Yarn elongation at break (%)	11.2	13.1
Weft stops/1000 picks	0.44	0.16
Warp stops/1000 picks	0.68	0.25
Overall weaving efficiency (%)	90.9	97.8

Shade: 0.35% Lanacron Yellow S2G; 0.2% Lanacron Red SG; 4.1% Lanaset Navy R

The Sirolan-LTD process for dyeing wool at sub-boil temperatures is in commercial use in Australasia and is currently being introduced into Asian and European dye houses.

Dyeing for a short time at the boil

As discussed above, work carried out since the launch of the Sirolan-LTD low temperature dyeing process has shown that Valsol LTA-N can also be used to dye all types of wool substrates to satisfactory standards by employing significantly shorter times at the boil compared with other methods. As shown in Figure 1, the procedure used for the short-time-at-the-boil method is similar to that used for the low temperature process, except that the dye bath is heated to 100°C instead of 85–90°C. The time required at the maximum temperature is determined by the type of dyes and depth of shade. Industrial experience has shown that dyed materials of equivalent fastness and dyeing quality to those produced by conventional methods, can be obtained with boiling times around 30–50% of the times recommended for the corresponding conventional procedures. The comparison of typical conventional and Sirolan-LTD short-time-at-the-boil dyeing cycles in Figure 2 shows that the Sirolan-LTD method gives a significant reduction in dyeing time, compared with the conventional method. This can lead to marked improvements in dye house productivity, in addition to the other benefits of high dye bath exhaustion, good macro-levelness and excellent coverage of tippiness, discussed above. In accord with the results in Table I, the data in Table IV show that the dyefastness properties of a worsted yarn (l/40 Nm) dyed to a full shade by the short-time-at-the-boil method were comparable with the fastness properties of the shade dyed for a longer time by the conventional procedure. Table IV also

shows that the colour yield, as measured by the colour difference (AE), was similar to that obtained by the normal method. Decreasing the time at the boil gave less fibre damage than was produced by conventional dyeing. Thus, in Table IV the tenacity, elongation at break and work to break of the single yarns were higher for the material dyed by the Sirolan-LTD method for 20 minutes at the boil, than for the yarn dyed by the corresponding conventional cycle for 60 minutes at the same temperature. This version of the process is currently used by piece dyers.

Table IV - Dyefastness and physical properties of yarn dyed by conventional and Sirolan-LTD short-time-at-the-boil methods.

Dyeing method (IWS Fashion Shade W94.36)	Dyefastness						Physical properties			Colour difference
	Alkaline wet				Rubbing	Tenacity	Elongation	Work to		$(,\backslash E)$ (b)
(a)	Contact							Break		
	(IWSTM174)				(IWSTM165)	(cN/tex)	%	(cN.cm)		
	Wo	Ny	Co	Dry	Wet					
Convent. 60 min. at 100°C	4-5	4	4-5	4-5	3-4	6.2 (87)	10.2 (68)	638 (59)		
Sirolan-LTD 20 min. at 100°C	4-5	4	4-5	4-5	3-4	6.7 (94)	11.3 (75)	765 (71)	0.4	

(a)   *IWS Fashion Shade W94.36 obtained with a Lanaset combination (3.5% oww total dye concentration) by the conventional method and the Sirolan-LTD short-time-at-the-boil procedure.*

(b)   *Measured on a Datacolor Texflash.*
The numbers shown in parentheses for tenacity, elongation and work to break are the percentage of the value for the ecru yarn.

One application of the short-time-at-the-boil method worth noting is piece dyeing with Neolan P dyes. Excellent results have been obtained with boiling times of 30–45 minutes, instead of the 60–90 minutes recommended by the dye manufacturer's pattern card. It has been found that because of their relatively poor fibre covering properties, Neolan P and other types of 1:1 premetallised dyes require a slightly modified procedure. The wool should be pretreated at pH 8 with 3% oww Valsol LTA-N, for 15 minutes at 40°C. The dye bath is then set to pH 3.5 with formic acid and sodium sulphate. In order to obtain good coverage with 1:1 premetallised dyes, it is recommended that 8–10 % oww of sodium sulphate is used. As for other dyes, however, levelling agents other than Valsol LTA-N **must not** be used. These are unnecessary, even for Neolan P dyestuffs. Dyestuff fastness on fabrics dyed with Valsol LTA-N for a short-time-at-the-boil have been found to be similar to those on fabrics dyed for longer times at the boil, by the normal method.

Table V - Wet-burst strength of Barathea fabric dyed with Neolan P dyestuffs by:

Conventional and Sirolan-LTD	Short-time-at-the-boll methods
Dyeing method	Fabric wet-burst strength
	(% value for undyed fabric)
Conventional (90 min. at 1OO°C)	78
Sirolan-LTD (30 min. at 1OO°C)	89

Shade: 3.5% Neolan Red P, 2. 0% Neolan Blue P, 1. 5% Neolan Yellow P.

The wet-burst strength results in Table V shows that fibre damage can be significantly reduced by using the Sirolan-LTD method to dye wool fabrics at the boil for a shorter time than used in other procedures. It is expected that this method will be used whenever improvements in dvehouse productivity are of high priority.

Conclusion

This paper describes the Sirolan-LTD process, a new method of dyeing all types of wool substrates, either for the usual time at a sub-boil temperature, or for a short-time-at-the-boil. The key to the process is a special auxiliary (Valsol LTA-N), jointly developed by the CSIRO Division of Wool Technology and ICI Valchem (Australia). Advantages of both new procedures include excellent coverage of tippiness, with a wide range of dyes, and high exhaustion levels of dyestuffs and insect-resist agents. The improved dye bath exhaustion over conventional dyeing processes can result in a reduction in effluent load. Wool dyed by the Sirolan-LTD process has been shown to have the fastness properties of conventionally-dyed material. Both the low temperature and the short-time-at-the-boil methods give a lower degree of fibre damage, and hence improved processing performance of the dyed wool compared with other dyeing procedures. The short-time-at-the-boil dyeing route offers the additional advantage of increased productivity in the dye house.

Acknowledgment

References

1. J.D. Leeder, J.A. Rippon, F.E. Rothery, 1.W. Stapleton, Proe 7th Int. Wool Text. Res. Conf., Tokyo, 1985, V, p.99-108.

2. J. A. Rippon, Chapter 1. 'The Structure of Wool' in 'Wool Dyeing'. Ed. D.M. Lewis. Publ. Soc. Dyers and Colourists, Bradford, 1992. p.1-51.

3. J.A. Rippon, F.J. Harrigan Proe 8th Int. Wool Text. Res. Conf., Christchurch, 1990, IV, P.50-59.

4. J.A. Rippon, F.J. Harrigan, International Dyer, July 1994, p.20-25.

5. M.G. Huson, Textile Res. J., 1992, 62, p.9-14.

6. J.D. Leeder, J.A. Rippon and D.E. Rivett, Proc. 7th Int. Wool Text, Res. Conf., Tokyo, 1985. IV, p.312-321.

7. K. Joko, J. Koga and N. Kuroki, Proc. 7th Int. Wool Text. Res. Conf., Tokyo, 1985, V, p.23-32.

8, H. Baumann and L.D.Setiawan, Proc. 7th Int. Wool Text. Res. Conf., Tokyo, 1985, V, p.1-10

9. J.A. Rippon, F.J. Harrigan, Proc.13th Int. Symposium, Soc. Dyers and Col. ANZ, Christchurch, Oct. 1992.

7.2 The Basolan® AS process: a new concept in wool dyeing

P.G. Cookson, P.R. Brady and K.W. Fincher
CSIRO Division of Wool Technology
Geelong Laboratory
P.O. Box 21
Belmont, Victoria 3216, Australia.

P.A. Duffield and S.M. Smith
IWS Development Centre
Valley Drive
Ilkley, West Yorkshire LS29 8PB, England.

K. Reincke and J. Schreiber
BASF Aktiengesellschaft, ETM/H - H 201
67056 Ludwigshafen, Germany.

Summary

The Basolan AS process is a new approach to dyeing wool. The process restricts the deterioration of wool properties which occurs as a result of dyeing. This is achieved through a reduction in the extent to which wool is permanently set during dyeing. Two options are available to the dyer, and all that is involved is the addition of anti-setting chemicals to the wool dye bath. Processing and product benefits can be obtained for wool dyed as loose fibre, top, yarn (package or hank), and woven fabric by using Basolan AS.

Introduction

Permanent setting of wool occurs during dyeing, and this has a detrimental effect on the properties of the fibre. Studies have been carried out over a number of years at the Geelong Laboratories of CSIRO Division of Wool Technology, and at the IWS Development Centre in Ilkley, in order to minimise this problem. The result of this intensive work is the Basolan AS Process for dyeing wool. Industrial trials carried out over the past three years have established significant processing and product benefits for wool that has been Basolan AS-dyed in the form of loose fibre, top, yarn and piece goods. Two options are available to the dyer. Commercialisation of the process is being carried out by BASF.

This paper describes permanent setting, and the adverse effects it has on the properties of dyed wool. It gives details of the two alternative procedures that make up the Basolan AS Process, and the results of industrial trials.

Permanent setting during dyeing

Investigations by the CSIRO Division of Wool Technology have established that permanent setting is a major reason for the deterioration in the physical properties of the wool fibre which can occur as a result of dyeing [1–6]. Permanent setting during dyeing is a contributory factor to a reduction in the tensile strength of fibres, yarns and fabrics. It is also the main cause of the increased hygral expansion of fabric as a result of piece dyeing, and the reduced bulk of package-dyed yarn.

Chemical origin

Permanent setting of wool takes place through rearrangement of disulphide bonds. This reaction requires the presence of thiolate anions, which are formed by deprotonation of cysteine thiol groups (Equations 1 and 2).

$$\text{Wool-SH} \; \rightleftharpoons \; \text{Wool-S}^- + \text{H}^+ \qquad \textbf{(1)}$$

$$\text{Wool-}S_a\text{-}S_b\text{-Wool} + \text{Wool-}S_c^- \rightleftharpoons \text{Wool-}S_a^- + \text{Wool-}S_b\text{-}S_c\text{-Wool} \qquad (2)$$
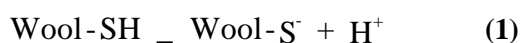
Cysteine thiol occurs naturally in untreated wool, and is also produced as an intermediate in the hydrolytic decomposition of cystine residues [7, 8]. Significant thiol-disulphide rearrangement occurs in boiling water after several minutes at pH 4.5 [3]. Permanent setting increases with dyeing pH and temperature (Figure 1), and also with dyeing time (Figure 2) [3,9-11].
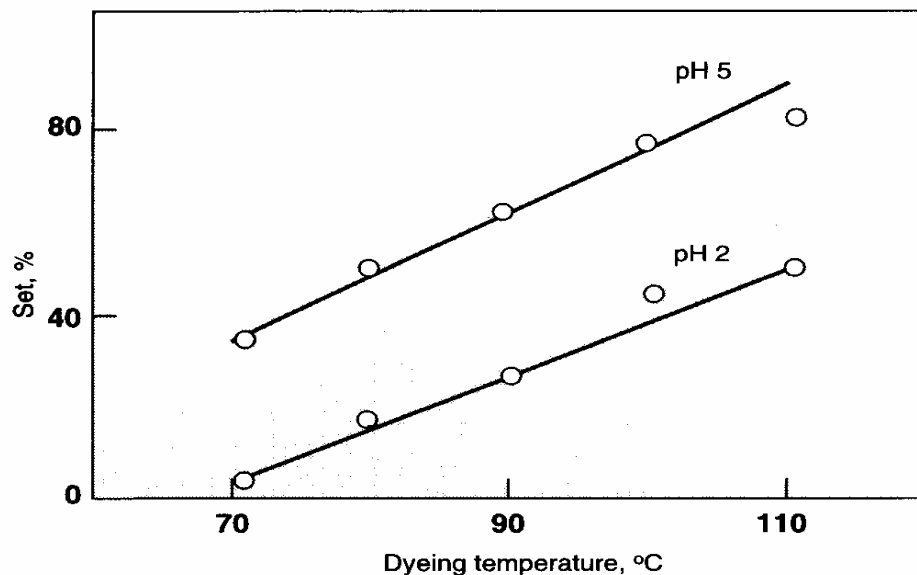
Figure 1 Relationship between dyeing conditions and permanent set (for a dyeing time of 1 h at maximum temperature)
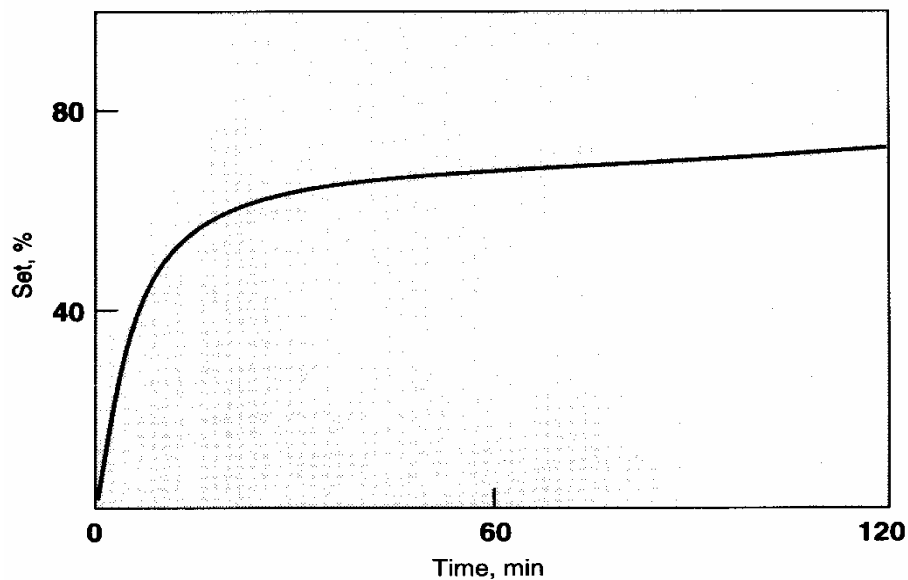
Figure 2 Relationship between permanent set and dyeing time at 100°C (pH 4.5)

Measurement

The level of permanent set induced by dyeing can be conveniently assessed by the crease-angle method [1, 12]. Prior to dyeing, a crease is pressed into a small sample of a woven fabric. This fabric would normally be an undyed, pure wool fabric that has been prepared for piece dyeing. The crease should run along either the warp or weft direction.

Following pressing, it is necessary to stitch the fabric in order to hold the crease in place during dyeing. This is done by inserting one line of stitching approximately 1 mm from, and parallel to, the creased edge, and another approximately 1 cm from the edge.

After dyeing, the stitching is removed. The fabric on both sides of the crease is cut 5–10 mm from, and parallel to, the creased edge. The V-shaped snippets of yarn (about 10–20) are carefully removed from the crease, relaxed in water at 70°C for 30 minutes, and the average angle, a, between the 'legs' of the snippets is measured. The level of permanent set is calculated according to the equation in the Figure 3. As the level of permanent set increases, the angle, a, decreases. For the example of the normal dyeing illustrated in Figure 3, a = 45° and set is calculated to be 75%.

$$\text{Set (\%)} = \frac{180 - \alpha}{180} \times 100$$

Figure 3.

Fibre damage

Damage to the wool fibre as a result of dyeing is normally attributed to chemical degradation of the fibre [7, 8, 13, 14]. At low pH values (1.8–3.0), degradation occurs predominantly through hydrolysis of the amide bonds in the polypeptide chains (Equation 3). Hydrolysis of disulphide cross-links between the polypeptide chains occurs at higher pH values (Equation 4). Minimal wool damage has been reported to occur when dyeing in the pH range 3–5 [13]. This has been explained by stabilisation of the structure of the wool proteins within the isoelectric region (pH 3.5–4.5) of the fibre. Under these conditions, the concentration of salt linkages is at a maximum, and hydrolysis of amide and disulphide bonds is minimised.

$$—CH(R^1)—CONH—CH(R^2)— \ + \ H_3O^+$$
$$\downarrow$$
$$—CH(R^1)CO_2H \ + \ H_3N^+—CH(R^2)—$$

Equation 3.

$$R^3(H)—CH_2—S—S—CH_2—R^4(H) \ + \ H_2O$$
$$\downarrow$$
$$R^3(H)—CH_2—SOH \ + \ R^4{=}CH_2 \ + \ H_2S$$
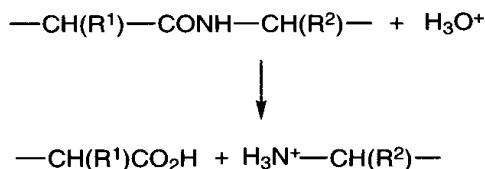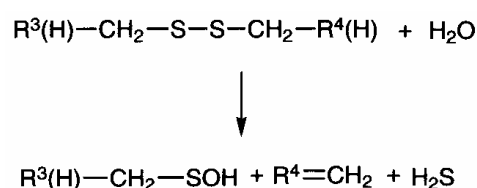
Equation 4.

Permanent setting is also a major factor responsible for the impairment of the tensile properties of the wool fibre as a result of dyeing. The following theory has been proposed to explain this behaviour [6]. The polypeptide chains in a ***straight***, unstrained wool fibre are able to become load-bearing simultaneously during tensile testing, resulting in a relatively strong fibre (Figure 4). If a straight wool fibre is strained into a ***bent*** configuration prior to dyeing, the chains on the outside of the curve become extended, and those on the inside of the curve are compressed. Thiol-disulphide rearrangement during dyeing allows the strained chains to rearrange into more uniform, unstrained states, similar to those in the straight fibre. The curved configuration of the fibre is now its stable form.

If the dyed, curved fibre is straightened, the polypeptide chains that were on the outside of the curve are compressed, and those that were on the inside of the curve are extended. The work required to break the fibre is somewhat less than for the original, straight fibre, since

the chains are no longer acting together to resist the applied force. The chains that were on the inside of the fibre become load-bearing first, and this causes premature failure in a tensile test. This behaviour is of practical significance since wool fibres prior to dyeing are often distorted from their natural configurations. For example, the fibres in a yarn are bent into helical configurations due to the yarn twist, and the fibres in a fabric are further bent because of the weave crimp that is superimposed onto the yarns.
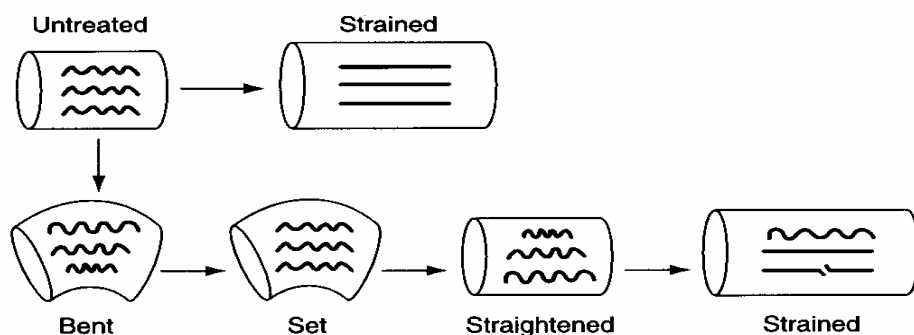
Figure 4 Effect of setting and curvature on the tensile failure properties of wool fibres

Increased hygral expansion of piece-dyed fabric

Hygral expansion refers to the dimensional changes that occur in a relaxed, pure wool fabric as the moisture content is changed [15]. Most finished wool fabrics increase in dimensions as the moisture content is increased. This phenomenon is reversible, and contraction occurs on drying. The hygral expansion of a fabric is calculated from the difference between the wet length and the dry length, expressed as a percentage of the dry length.

The effect of dyeing - and permanent setting – on hygral expansion is illustrated quantitatively by the following example. Curve A in Figure 5 shows the relationship between the warp fabric length and moisture content for a relaxed, gabardine fabric that has been semi-decatised as a preparation for piece dyeing [10, 11]. The (warp) hygral expansion of the fabric before dyeing was 4.5%. After dyeing for two hours at the boil, the level of permanent set was 75%, and the hygral expansion changed dramatically, as shown by curve B. Although the wet dimension remained unaltered, the dry dimension was considerably less than in the undyed fabric, and the hygral expansion increased to 10.1%.

The hygral expansion of a fabric increases when the *fabric itself* is subjected to a permanent- setting operation, for example, piece dyeing or pressure decatising. For a given fabric, hygral expansion increases as the level of permanent set increases. Levels of set introduced during dyeing are normally higher than those resulting from fabric preparation and finishing procedures. Piece-dyed fabrics, therefore, usually have the highest levels of hygral expansion.

Permanent setting of a fabric stabilises the yarns in the bent conformations imposed by the weave structure, that is, the weave crimp is permanently set into the yarns. This has the effect of reducing the forces that act between warp and weft yarns at their points of contact, and increases the tendency for the fabric to contract on drying (see curve B in Figure 5) [15]. Increases in hygral expansion that occur as a result of piece dyeing and finishing are also influenced by the weave structure. Fabrics with high levels of weave crimp - such as gabardine fabrics in the warp direction - are most likely to develop high levels of hygral expansion [16].
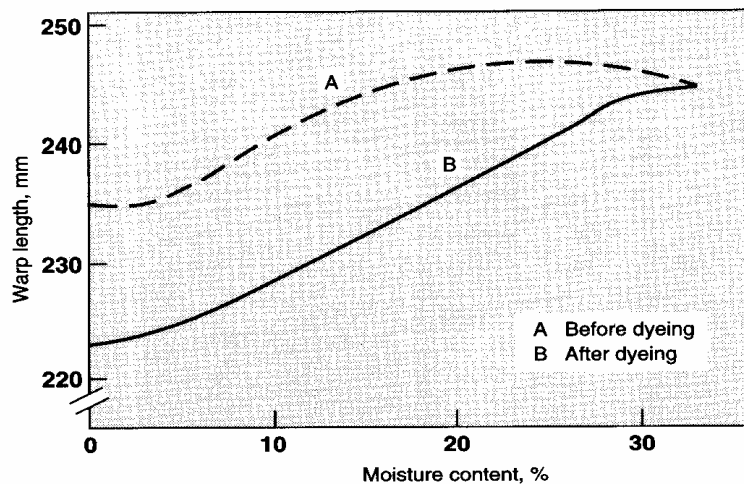
Figure 5 Effect of dyeing on the hygral expansion of a 2/1 twill gabardine fabric

It has often been assumed that setting 'stabilises' a wool fabric, and to a certain extent this is correct. For example, pressure decatising is used to impart a flat, uniform and permanent surface finish to a wool fabric. Permanent setting, however, also increases the tendency for the dimensions of a fabric to change with regain, as discussed above. In this respect, setting has a destabilising influence [17].

Hygral expansion values in excess of 5–6% in either warp or weft direction can lead to appearance problems in structured pure wool garments at high relative humidities [10, 11, 18]. Tailored jackets are usually constructed under conditions in which the fabric moisture content is in the range 2–10%, whereas in wear, the moisture content may rise to 20% under humid conditions, or as high as 34% if the garment becomes wet. As garments absorb moisture in excess of that present when they were made, the inextensible parts, such as seams and interlinings, remain fixed. However, in other parts of the garment, the fabric will be free to increase in length. This differential dimensional behaviour leads to puckering in those areas adjacent to seams and fused interlinings at high relative humidities, as shown in Figure 6.
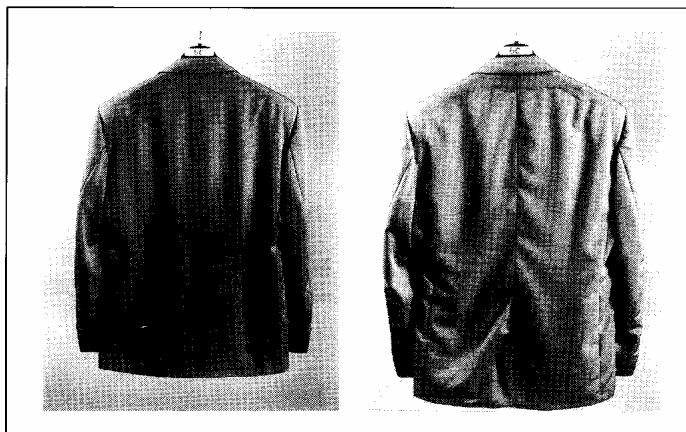
Figure 6 Effect of hygral expansion on the appearance of a men's jacket made up from a piece-dyed gabardine fabric with a warp hygral expansion of 10.1%; the picture on the left figure shows the garment after pressing and conditioning to 65% RH (20°C), and the one on right shows the same garment after spraying with a light mist of water

Reduced bulk of package-dyed yarn [4]

Yarn in packages is stretched because of the tensions experienced in winding. As a result, yarn bulk is reduced significantly. Permanent setting that occurs during dyeing stabilises the yarn in its stretched conformation, resulting in a permanent reduction in bulk. The axial compression of yarn packages in commercial dyeing machines can lead to an additional loss of bulk. Package dyeing can also cause yarn to become permanently flattened and distorted at those points where different parts of the yarn are in contact with each other. These deformations can detract from the appearance of a knitted garment.

Drying of packages causes the yarn to become cohesively (that is, temporarily) set. Cohesive setting alone can maintain the yarn in its stretched configuration after dyeing. However, the effects of cohesive setting can be removed by an appropriate, post-dyeing relaxation procedure, such as single-end drying without tension. In order to assess the permanent loss of bulk which occurs as a result of package dyeing, it is necessary to carry out an appropriate relaxation treatment to remove the effects of cohesive setting.

Reported methods for restricting permanent setting

Permanent setting during dyeing can be restricted by adding an ***anti-setting agent*** to the dye bath. Anti-setting agents are chemicals that react with thiol groups in wool, thus inhibiting the thiol-disulphide interchange reaction. Oxidants such as hydrogen peroxide and potassium bromate are effective anti-setting agents [1, 2, 4–6], but cause unacceptable yellowing of the wool and interact with the chromophores of a number of dyes. Potassium bromate is effective at low pH values, but has little or no effect at high pH values [5]. Other anti-setting agents include formaldehyde and chloroacetamide [1], Sandospace® R (Sandoz) [19], copper(II) and cobalt(II) salts [19], and reactive dyes containing the a-bromoacrylamido group [20, 21].

The following benefits have been reported for wool dyed in the presence of anti-setting agent:

- improved fibre, yarn and fabric tensile properties

- reduced fabric hygral expansion

- increased bulk of package-dyed yarn.

When using an anti-setting agent, it is not possible to completely prevent permanent setting of wool. However, considerable benefits can be obtained if the level of permanent set is reduced by half, or even less. The level of set for normal wool dyeing may be as high as 70–80%, and this may be reduced to approximately 30–40% with an anti-setting agent (see Figure 3). It has been reported that significant improvements in the properties of dyed wool can be obtained if the level of permanent set is restricted to no more than 40–50% [3, 9].

The Basolan AS process

The Basolan AS process has been developed to provide the dyer with two commercially-viable options for minimising permanent setting:

- The most generally-applicable procedure involves the use of the liquid product, Basolan AS-A, together with hydrogen peroxide. Basolan AS-A is a peroxide activator that also reacts with wool. It enhances the anti-setting effect of the peroxide at lower pH values, and reduces yellowing of the wool. This procedure is recommended for use with those dyes that are not sensitive to hydrogen peroxide, and this includes the majority of wool dyes. Basolan AS-A is supplied by BASF.

- A procedure is still in the development stage for application with dyes that are sensitive to hydrogen peroxide, and involves the use of Basolan 2458. This procedure

is especially suited to dyeing at pH values of 4.5, or lower. Basolan 2458 is an acidic product in powder form which reacts with the wool fibre. It is not an oxidising agent, and does not rely on the addition of oxidants. It is recommended for use with all 1:1 metal-complex dyes, and with afterchrome dyes that are sensitive to hydrogen peroxide.

Basolan AS-A + Hydrogen peroxide

Application

This procedure can be used over the entire pH range at which wool is dyed, and the standard recommendation is illustrated in Figure 7. The dye bath is set at the normal starting temperature with 0.5 g/l Basolan AS-A, and run for about five minutes. One ml/l hydrogen peroxide (35%) is added next, and run for about 5–10 minutes. Adjustment of the pH may commence during this step. The dyeing is then continued in the normal manner with the addition of auxiliaries and dyes. The technique is applicable for maximum dyeing temperatures in the range 85–110°C.

The amounts of Basolan AS-A and hydrogen peroxide (35%) used should not be less than 1% and 2% (o.w.f.), respectively. This means that at liquor ratios of less than 20:1, the concentrations required will be greater than those indicated in Figure 7. The ratio of Basolan AS-A to hydrogen peroxide (35%) should always be 1:2 (w/v). Although there is an increased tendency for setting to occur at higher pH values, optimum results should be obtained by following these guidelines. If dyeing times are extended for shading additions, 0.25 g/l (or 0.5%) of hydrogen peroxide (35%) should be added to the bath prior to each extra addition of dye; further additions of Basolan AS-A are not required. If it is necessary to re-dye fabric in a fresh bath, the Basolan AS-A and hydrogen peroxide need to be added again to the dye bath in the recommended amounts. For dyeings at pH 6 or higher, the presence of hydrogen peroxide may lead to a gradual drop in the dye bath pH. By setting the initial pH of the dye bath at about half a unit higher than normal, this effect can be offset.
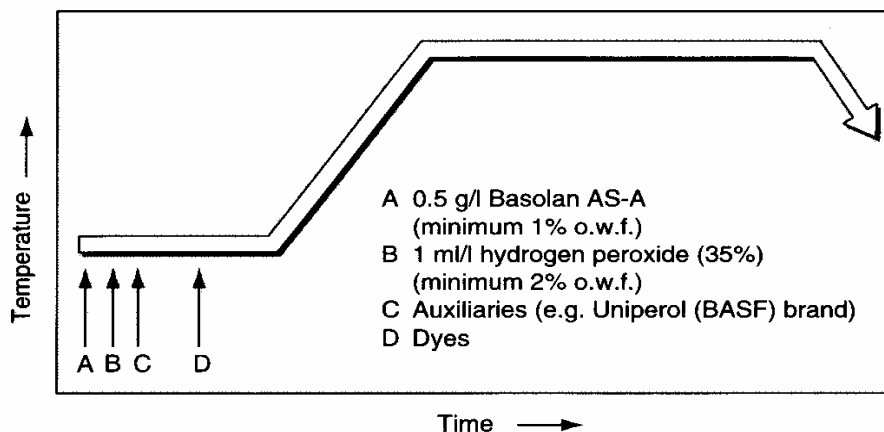

A 0.5 g/l Basolan AS-A
   (minimum 1% o.w.f.)
B 1 ml/l hydrogen peroxide (35%)
   (minimum 2% o.w.f.)
C Auxiliaries (e.g. Uniperol (BASF) brand)
D Dyes

Figure 7 Profile for dyeing with Basolan AS-A + hydrogen peroxide

Brighter shades

Compared with conventional wool dyeing, there is less yellowing and greying of the base fibre. Pale and medium shades are noticeably brighter. Most dyes have a higher saturation value (positive chroma difference, ?C) and a smaller grey component (positive lightness difference, ?L) when compared with normal dyeings. Existing dye recipes must be checked, and adjusted if necessary. Dyeing levelness is not adversely affected.

Dye compatibility

Test method

The Basolan AS-A/hydrogen peroxide procedure can be used in conjunction with the majority of acid-levelling, 1:2 metal-complex, milling and reactive dyes where there are no interactions between hydrogen peroxide and the dye chromophores.

IWS and BASF have examined an extensive range of dyes for their sensitivity to peroxide. The following test conditions were used:

Fabric: Pure wool serge

Liquor ratio: 40:1

Initial dyeing temperature: 25–30^{0}C

Add 0.5 g/l Basolan AS-A

1.0 ml/l hydrogen peroxide (35%)

Dyes and auxiliaries as normal

Procedure: Raise temperature to 98°C at 1°C per minute, boil for 60 minutes, cool, rinse.

Control dyeings were carried out in the same manner, but without Basolan AS-A and hydrogen peroxide. Dye concentrations corresponding to approximately 1/3 standard depth were generally used, since dye/peroxide sensitivity is more apparent at lower dye concentrations. Black and navy dyeings were carried out using the recommended dyestuff levels to produce the required shades. When recommended as trichromatic components for mixture shades, navy dyes were also assessed at 1/3 standard depth.

The Basolan AS-A/hydrogen peroxide procedure is considered suitable for use with those dyes that give a similar or higher saturation value and a similar hue (? H) for a Basolan AS-A/hydrogen peroxide dyeing in relation to a control dyeing. It was concluded from these tests that this includes the majority, but not all, of wool dyes. For a number of dyes, the shades obtained for the Basolan AS-A/hydrogen peroxide procedure are weaker (negative ? C) and/or different in hue to those of normal dyeings.

Information will be made available concerning those dyes from the Western dyestuff manufacturers for which the Basolan AS-A/hydrogen peroxide procedure is unsuitable. The use of Basolan 2458 is recommended for these dyes. The suitability of the Basolan AS-A/hydrogen peroxide procedure for all other dyes must be checked under local conditions. Because of the large number of factors that can affect the results, users must conduct their own tests and trials. It is essential that dye recipes are checked before proceeding to large-scale trials.

1:2 Metal-complex dyes

Basolan AS-A/hydrogen peroxide can be used with the vast majority of 1:2 metal-complex dyes, both sulphonated and non-sulphonated. BASF recommend use of the following Acidol® dyes – 1:2 metal-complex dyes and associated dyes for brighter shades – with this procedure:

Acidol®	Yellow KM-F	Brilliant Yellow M-5GL	Black M-SRL
	Red KM-S	Brilliant Yellow M-3GL	Black M-SGL
	Bordeaux KM-B	Yellow M-2GLN	
	Olive KM-G	Yellow M-5RL	

Brown KM-N	Orange M-RL
Scarlet M-L	
Yellow KW-A	Red M-BR
Red KW-E	Dark Blue M-TR (as Navy Blue)
Blue KW-I	Brilliant Blue M-5G.

As mentioned above, shades of pale and medium depth will generally be brighter than normal, and it may be necessary to adjust dye recipes. Basolan 2458 is recommended for the small number of 1:2 metal-complex dyes which undergo changes in depth and dyeing shade in the presence of hydrogen peroxide.

Afterchrome dyes

Most afterchrome dyes are sensitive to hydrogen peroxide, and the use of Basolan 2458 is recommended. However, the Basolan AS-A/hydrogen peroxide procedure is now used commercially for the dyeing of loose fibre, top and fabric with C.I. Mordant Black 9.

When dyeing with chrome dyes, the Basolan AS-A and hydrogen peroxide are added to the dyeing bath before the addition of auxiliaries and dyes. 'Low-chrome' methods based on Glauber's Salt (Bayer) and Lyocol® CR (Sandoz) [22] are compatible with the Basolan AS-A/hydrogen peroxide procedure. However, any dyeing operation employing the addition of sodium thiosulphate to the chroming bath should be avoided, since this chemical is a setting agent. Fresh-bath chroming is recommended, since chroming in the exhausted dye bath leads to increased levels of residual chromium.

C.I. Mordant Black 9 is often formulated with shading components. In this situation especially, the Basolan AS-A/hydrogen peroxide procedure must be examined carefully for suitability of use with the formulated dyestuff.

Reactive dyes

Basolan AS-A/hydrogen peroxide is recommended for use with most reactive dyes.

The amino groups in the wool fibre are the most common binding sites for reactive dyes [23]. Although the free thiol content of wool is relatively low, the cysteine thiol groups (which are more reactive than the amino groups) are also potential sites for reaction with reactive dyes. The established anti-setting behaviour of reactive dyes is indicative of reaction with cysteine thiol [20,21], although results from the present study have shown that this effect varies considerably with individual dyes in the same dye range. A reduction in the number of thiol binding sites, through reaction with hydrogen peroxide, could adversely affect dye fastness, but laboratory studies have shown no significant effects on fastness for dyestuff levels up to 3% (o.w.f.). Dye fastness should be checked, however, especially for higher dyestuff levels. For dyeings with reactive dyes in the presence of 1 g/l hydrogen peroxide, Ciba have reported a reduced rate of fixation (with no effect on the degree of final fixation) and excellent levelness [24].

When an alkaline after-treatment is required to improve the fastness of reactive dyes, 1 ml/l of hydrogen peroxide (35%) should be added to the after-treatment bath (prior to pH adjustment) in order to restrict the development of further setting. Addition of Basolan AS-A to the after-treatment bath is not essential. After-treatments based on the combination of hydrogen peroxide with ammonia or sodium carbonate are equally effective. As an alternative to an alkaline after-treatment at 80°C, wet fastness can be improved by using Basolan F at 40°C.

Basolan 2458

Basolan 2458 restricts the setting of wool during dyeing without the addition of an oxidising agent. As the costs are somewhat higher than for Basolan AS-A, it is preferred for only those dyes for which the Basolan AS-A/hydrogen peroxide procedure is unsuitable. The anti-setting effectiveness of Basolan 2458 is considerably better at lower pH values, and best results are obtained at pH 4.5, or below. The use of Basolan 2458 is recommended especially for 1:1 metal-complex dyes (for example, Palatin® Fast) and afterchrome dyes. On the basis of our present knowledge, Basolan 2458 has little effect on the dyeing process or the dyed shade.

The use of Basolan 2458 is relatively simple. The product can be treated in essentially the same manner as a dyeing auxiliary or acid, without any extension to the dyeing cycle. When using 1:1 metal-complex dyes at lower pH values, 2 g/l of Basolan 2458 should be added directly to the dye bath at the start of the dyeing, together with the usual auxiliaries. The required amounts of sulphuric acid or formic acid to obtain a given pH value will be less than normal. The use of 3 g/l of the product is recommended when dyeing at higher pH values with, for example, afterchrome dyes. In this situation, partial neutralisation of the Basolan 2458 with caustic soda before addition to the dye bath will generally be necessary in order to avoid a pH that is too low.

Basolan 2458 is already available from BASF, but industrial evaluation is still in its early stages. It is intended to re-name the product as Basolan AS-B on conclusion of these trials.

Results of industrial trials with Basolan AS-A + hydrogen peroxide

Industrial trials of the Basolan AS-A/hydrogen peroxide procedure have been carried out in seven different countries over the past three years. In all of the examples detailed below, trials were carried out using 0.5 g/l Basolan AS-A and 1 ml/l of hydrogen peroxide (35%) in standard dyeing cycles. Benefits have been observed for wool dyed in the form of loose fibre, yarn, top and piece goods.

Loose-fibre dyeing

The substrates used were 30 micron wool of commercial 'Shetland' quality, and 22.5 micron wool (Bradford-combed broken top) of commercial 'lambswool' quality. Basolan AS and control (that is, normal) dyeings were performed in conical-pan machines, with individual dye lots ranging from 75 to 400 kilograms.

A fresh-bath, afterchrome procedure was used, the dye recipe being based on C.I. Mordant Black 9. Dyeing was carried out for 30 minutes at 85^0C (pH 4.5), followed by 20 minutes at 95^0C (pH 3.5). Chroming was carried out for 35 minutes at 95^0C (pH 3.5–4.0).

The Basolan AS-dyed and control-dyed Shetland (three tonnes) were processed separately through the same woollen card set, and were spun to 2/9 Nm yarn on a ring frame. The dyed lambswool (three tonnes) was processed to 2/17 Nm yarn. The number of end-breaks in spinning for the Basolan AS-dyed fibre was reduced by 17% for the lambswool, and 30% for the Shetland. Increases in yarn tenacity and extension were observed (Table 1). The company involved in these trials has been using the Basolan AS Process on a commercial basis for an extended period, and the improvements in spinning have been consistent.

Top dyeing

Basolan AS and control dyeings were each carried out using 1500 kilograms of 21 micron wool. A fresh-bath, afterchrome procedure was used, the dye recipe being based on C.I. Mordant Black 9. Dyeing was carried out for 15 minutes at 98°C [3% acetic acid (60%) – pH 4.1], followed by 10 minutes at 85°C [additional 1% formic acid]. Chroming was

carried out for 15 minutes at 90°C (0.5% formic acid), followed by 25 minutes at 90°C (additional 1% formic acid).

The same spinning lubricant was used for both the Basolan AS-dyed and control-dyed fibre, and the two lots were processed one after the other on the same machine. The fibre was spun to a count of 1/52 Nm. A spindle speed of 8650 r.p.m. was used for the Basolan AS-dyed fibre. For the control-dyed fibre, a lower speed of 8200 r.p.m. was required because of inferior running performance. A 36% reduction in end-breaks in spinning was observed for the Basolan AS-dyed fibre, in spite of the higher spindle speed. Increases in tenacity and extension were observed for the processed top, and increases in strength and extension were observed for the two-fold yarn (Table 2).

Package dyeing

(a)   2/72 Nm and 2/80 Nm yarn packages were Basolan AS-dyed and control-dyed with 1:2 metal-complex dyes. In each dyeing, seven packages – one on top of the other, and as close to identical as possible – were used, with the same degree of press packing. After drying and conditioning, the superior bulk of the Basolan AS-dyed yarn, which was judged subjectively to be softer, was evident (see Figure 8). In comparison with the control-dyed yarn, the Basolan AS-dyed yarn showed increases in strength and elongation of 19% and 47%, respectively, for the 2/72 Nm yarn, and of 12% and 32% for the 2/80 yarn.

(b)   One-kilogram packages of 2/48 Nm knitting yarn and 2/56 Nm weaving yarn were Basolan AS-dyed and control-dyed using acid-levelling, milling, 1:2 metal-complex and afterchrome dyes. The dyeing conditions were as follows:

- acid-levelling dyes: pH 2.5, 45 minutes at 100°C

- milling dyes: pH 4.5, 40 minutes at 100°C

- 1:2 metal-complex dyes: pH 6.0, 40 minutes at 100°C.

- afterchrome dyes: same-bath procedure, dyeing at pH 4.5 for 40 minutes at 100°C, chroming (at the same pH) for 20 minutes at 100°C.

Small improvements in yarn strength, and considerable increases in yarn extension, were observed for the Basolan AS-dyed yarn (Table 3).

Table 3

(c)   Two one-kilogram packages of 2/32 Nm knitting yarn (density, 0.28 g/cm^3) were Basolan AS-dyed and control-dyed with milling dyes for 30 minutes at the boil (pH 4.5–5.0). A set of typical results is presented in Table 4. The extension and bulk properties for the Basolan AS-dyed yarn were superior to those of conventionally package-dyed yarn, and comparable to those of conventionally hank-dyed yarn.

Table 4

Two weaving yarns of different count – 2/60 Nm and 2/80 Nm – were Basolan AS-dyed and control-dyed with 1:2 metal-complex and afterchrome dyes. The 2/80 Nm yarn, together with a 2/96 Nm yarn, were also produced from top that had been Basolan AS-dyed and control-dyed with afterchrome dyes. Increases in strength (8–19%) and extension (32-51%) were observed for both the packages and top that had been dyed using Basolan AS. The weaving characteristics of the yarns were assessed from 40-yard weaving trials using a Sulzer projectile loom, and the results are presented in Table 5. Considerable increases in weaving efficiency (which was based on weaving time) were observed for the yarn packages dyed with Basolan AS. A somewhat smaller (but still significant) improvement was observed for the 2/96 Nm yarn that had been top-dyed using Basolan AS.
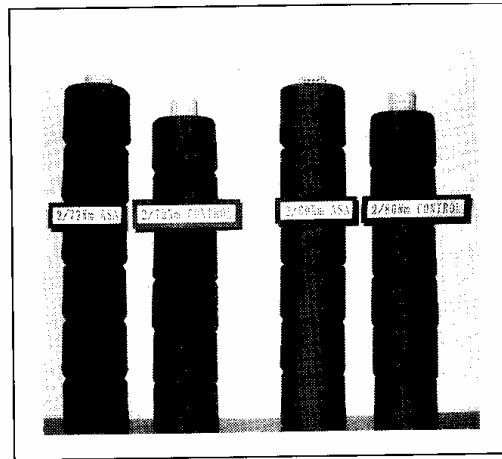
Figure 8 Effect of package dyeing (trial 1) on yarn bulk; from left to right 2/72 Nm (Basolan AS), 2/72 Nm (control), 2/80 Nm (Basolan AS), 2/80 Nm (control)

Hank dyeing

2/28 Nm woollen-spun lambswool machine-knitting yarn was Basolan AS-dyed and control- dyed with 1:2 metal-complex dyes for 30 minutes at the boil (pH 6.0). Plain-knit fabrics (cover factor 1.1) were made up from the dyed yarn, and were finished by scouring and drying. Increases in yarn extension and fabric thickness were observed for the Basolan AS-dyed yarn (Table 6).

Piece dyeing

(a) The following fabrics were Basolan AS-dyed and control-dyed as part of normal production:

  • Crespino – 95:5 wool/nylon, 2/1 twill with bi-component yarn (Sirofil) in the warp and 1/40 Nm pure wool yarn in the weft (175 g/m^2)

  • Sirofil – 90:10 wool/nylon, 2/1 twill with bi-component yarns warp and weft (145 g/m^2)

  • Gabardine (A) – 2/1 twill, 1/30 x 1/30 Nm (195 g/m^2)

  • Gabardine (B) – 2/1 twill, 2/60 x 2/60 Nm (225 g/m^2).

  Reductions in hygral expansion (Table 7) and increases in tear strength (Table 8) are apparent for the Basolan AS-dyed fabrics.

(b) A raised woollen fabric (1/7 x 1/7 Nm; 65% lambswool, 20% cashmere and 15% angora) was Basolan AS-dyed and control-dyed with acid-levelling dyes for 35 minutes at the boil (pH 4.5) in an experimental overflow machine. The control-dyed fabric showed severe running marks and uneven dyeing was evident in the creased areas. As a result, it was necessary to re-dye the fabric. Less severe running marks and a more uniform dyeing were observed for the Basolan AS-dyed fabric. Both fabrics were subjected to the same standard woollen finish. On the basis of subjective assessment, improved Fukurami (fullness) and Numeri (smoothness) were apparent for the finished Basolan AS-dyed fabric.

(c) A woollen plainweave fabric (2/16 x 2/16 Nm) and a worsted 2/1 twill gabardine fabric (2/64 x 1/34 Nm) were Basolan AS-dyed and control-dyed with acid-levelling dyes in an overflow machine. Significant reductions in running marks were observed with Basolan AS. The mill concerned has now Basolan AS-dyed 10,000 metres of the gabardine fabric and 8,000 metres of the woollen fabric as part of its normal

production. Furthermore, adoption of Basolan AS has enabled the use of a less severe setting operation prior to dyeing, and the elimination of a decatising operation after dyeing.

Further results and comments

Improved handle of knitwear

For many substrates produced from dyed fibre, top or yarn, the Basolan AS-dyed goods have been judged subjectively to be softer and bulkier. Loose-fibre dyeing with Basolan AS is being used commercially to improve the handle of cashmere and fine lambswool.

Reduced cockling of knitwear

Significant reductions in the cockling of knitted fabric produced from package-dyed worsted yarn have been observed.

Pilling

Studies carried out on knitted fabrics have not revealed any adverse effects of the Basolan AS-A/hydrogen peroxide procedure on pilling of knitwear. In one trial where a woven woollen fabric was piece dyed with Basolan AS, however, a reduced pilling performance was obtained.

Piece dyeing of woven fabric

The Basolan AS process has been adopted commercially for restricting increases in hygral expansion as a result of piece dyeing. The benefits are greatest for fabrics with a high level of weave crimp in either warp or weft direction. High levels of fabric setting before and/or after dyeing may negate these benefits. It is therefore important that both the finishing and dyeing operations are optimised to ensure the best results. In view of the reduced tendency for the development of permanent distortions during dyeing (for example, running marks), reduced setting before and/or after dyeing is an option that should be considered. A high level of flat setting prior to dyeing, however, may be appropriate in circumstances where hygral expansion is not a problem, and a fabric free from running marks is the primary objective.

There is generally little difference in handle for a finished fabric that has been dyed with Basolan AS, and one that has been dyed conventionally. In certain circumstances, however, Basolan AS-dyed fabric has been judged to have a slightly harsher handle, and one that is more akin to a top-dyed fabric than a piece-dyed fabric. This has been attributed to less milling and consolidation of the fabric during dyeing. In one particular trial, the desired handle was obtained by using an extended rope-scouring operation prior to dyeing.

Conventionally-dyed wool is easier to reset than wool that has been dyed using the Basolan AS Process. Levels of permanent set lower than normal have been measured as a result of pressure decatising Basolan AS-dyed fabric. This reduced ability to set dyed fabric has not caused any problems as a result of the industrial trials.

Conclusions

The benefits that can be obtained by using the Basolan AS-A/hydrogen peroxide procedure are as follows.

Wool dyed as loose fibre or top:

- Improved processing performance in carding and spinning

- Increased yarn elongation, leading to increased knitting and weaving efficiency

- Increased tensile properties of woven fabric

- Improved handle of knitted goods.

Wool dyed as yarn (package or hank):

- Increased yarn elongation, leading to increased knitting and weaving efficiency

- Increased bulk of knitting yarn

- Improved handle of knitted goods

- Reduced loop distortion in knitted fabric

- Increased tensile properties of woven fabric.

Wool dyed as woven fabric:

- Reduced hygral expansion, leading to improved garment appearance, with less puckering along seams

- Improved surface appearance, with less severe running marks

- Increased tensile strength and abrasion-resistance.

Shade brightening:

- Compared with conventional wool dyeing, there is less yellowing and greying of the base fibre; pale and medium shades are noticeably brighter.

- Slightly better light fastness because of the brighter base fibre.

Still being examined, or to be confirmed:

- Improved wool properties of wool/polyester blends dyed at high temperature

- Improved performance and appearance of carpets

- Reduced tippiness

- Accelerated drying of loose fibre and top

- Improved surface appearance of garment-dyed goods.

It is vital that the end-user assesses the advantages to be derived from the Basolan AS Process by examining his own materials and processing conditions. It is not possible to predict the magnitude of any benefits in individual circumstances, since there are many factors that can influence the end result.

In one package dyeing/weaving trial, a small improvement in the extension of a 1/60 Nm yarn – from 5.8% to 6.5% – was obtained with Basolan AS-A/hydrogen peroxide, yet there was a 47% reduction in the number of weft breaks on weaving. In another trial (see Table 2); however, an increase in the extension of a 2/52 Nm yarn from 12.2% to 19.0% with Basolan AS-A/hydrogen peroxide led to no significant improvement in weaving.

Especially in terms of processing performance, it is likely that the implications of the technology will be most important for those processors who are operating at or near the limits of their processing capabilities.

References

1. A.M. Wemyss and M.A. White, Proc. 3rd. Japan-Australia Joint Symposium on Objective Measurement, Kyoto (1985) 165.

2. J.R. Cook and B.E. Fleischfresser, Proc. 7th Int. Wool Text. Res. Conf. (Volume V), Tokyo (1985) 181.

3. P.R. Brady, P.G. Cookson, D.J. Evans and K.W. Fincher, Proc. Textile Institute 1988 Annual World Conference, Sydney (1988) 104.

4. J.R. Cook and B.E. Fleischfresser, *JSDC*, **105** (1989) 19.

5. P.G. Cookson, K.W. Fincher and P.R. Brady, *JSDC*, **107** (1991) 135.

6. M.G. Huson, *Textile Res. J.*, **62** (1992) 9.

7. D.M. Lewis, *Rev. Prog. Coloration*, **19** (1989) 49.

8. I. Steenken and H. Zahn, *JSDC*, **102** (1986) 269.

9. P.G. Cookson, A.G. De Boos, J.P. Nilon and A.M. Wemyss, Proc. Textile Institute 1988 Annual World Conference, Sydney (1988) 291.

10. P.G. Cookson, A.M. Wemyss and A. G. De Boos, Schriftenreihe des Deutschen Wollforschungsinstitutes, **108** (1991) 581.

11. P.G. Cookson, A.M. Wemyss and A.G. De Boos, *Melliand Textilber.*, **73** (1992) 522.

12. V. Køpke, *J. Textile Inst.*, **61** (1970) 361.

13. J.A. Rippon, in *Wool Dyeing,* Ed. D. M. Lewis (Bradford: Society of Dyers and Colourists, 1992) 1.

14. D.M. Lewis and S.M. Smith, *JSDC*, **107** (1991) 357.

15. P.G. Cookson, *Textile Res. J.*, **60** (1990) 579.

16. A.M. Wemyss and A.G. De Boos, *Textile Res. J.*, **61** (1991) 247.

17. T. Shaw, *Wool Science Review,* **55** (1978) 43.

18. P.G. Cookson and A.M. Wemyss, Proc. 8th Int. Wool Text. Res. Conf. (Volume V) Christchurch (1990), 380.

19. K. De Clerck, C.M. Carr and K.J. Dodd, *J. Textile Inst.*, **84** (1993) 611.

20. S.M. Smith, International Wool Secretariat, Ilkley, Laboratory Report No. C-338 (March, 1992).

21. K.J. Dodd, C.M. Carr and M. Baird, *JSDC*, **110** (1994)190.

22. P.A. Duffield, in *Wool Dyeing,* Ed. D.M. Lewis (Bradford: Society of Dyers and Colourists, 1992) 176.

23. D.M. Lewis, in *Wool Dyeing,* Ed. D.M. Lewis (Bradford: Society of Dyers and Colourists, 1992) 222.

24. K. Hannemann, *JSDC*, **108** (1992) 202.

Tables

Table 1: Results from loose-fibre dyeing trial.

Yarn property	Lambswool		Shetland	
	Control	**Basolan AS**	**Control**	**Basolan AS**
Strength (cN)	487	553	984	988
Extension (%)	10.4	11.4	9.1	10.5

Table 2: Results from top-dyeing trial.

Fibre/yarn property	Undyed	Control	Basolan AS
Tenacity (g/tex) (fibre)	9.86	7.30	8.82
Extension (%) (fibre)	50.2	38.2	43.3
Strength (cN) (yarn)	-	255	291
Extension (%) (yarn)	-	12.2	19.0

Table 3: Results from package-dyeing trial (b).

Dyes	Yarn	Strength (g)		Extension (%)	
		2/48 Nm	**2/56 Nm**	**2/48 Nm**	**2/56 Nm**
Undyed		290	306	14.8	26.4
Acid-levelling	Control	266	263	15.1	22.4
	Basolan AS	287	304	19.4	27.9
Milling	Control	250	242	12.5	16.9
	Basolan AS	276	294	18.2	26.0
1:2 Metal-complex	Control	248	232	11.3	12.9
	Basolan AS	278	281	16.6	23.3
Afterchrome	Control	260	261	12.4	19.3
	Basolan AS	276	252	16.5	20.5

Table 4: Results from package-dyeing trial (c).

Yarn	Strength (g)	Extension (%)	Bulk (cm^3/g)	
			After dyeing	**After dyeing and steaming**
Control	383.9	9.9	8.1	13.0
Basolan AS	346.2	12.3	8.7	14.3
Hank-dyed	363.5	12.3	10.9	14.3

Table 5: Results from package-dyeing trial (d).

Weaving property	Package-dyed						Top-dyed	
	Metal complex		Afterchrome					
	2/60 Nm		2/80 Nm				2/96 Nm	
	Control	**AS**	**Control**	**AS**	**Control**	**AS**	**Control**	**AS**
Fabric produced	Plainweave		2/1 Twill		Plainweave		2/1 Twill Gabardine	
Weaving efficiency (%)	71.9	90.2	69.0	86.4	95.1	96.3	87.1	93.1
End breaks — Warp/yard	1.19	0.05	1.60	0.61	0.09	0.11	0.55	0.39
End breaks — Weft/yard	0.29	0.12	0.24	0.28	0.06	0.03	0.13	0.17

Table 6: Results from hank-dyeing trial.

Yarn/fabric property	Control	Basolan AS
Strength (g) (Yarn)	253	241
Extension (%) (Yarn)	5.8	7.1
Thickness (mm) (Fabric)	2.45	2.68

Table 7. Hygral expansion results from piece-dyeing trial (a).

Fabric	Dyes	Hygral expansion (%)			
		Control		Basolan AS	
		Warp	Weft	Warp	Weft
Crespino	1:2 Metal-complex	3.32	3.63	2.72	3.01
Sirofil	Milling	5.37	4.12	2.58	2.84
Sirofil	Afterchrome	5.40	4.64	4.63	3.62
Gabardine (A)	Milling	3.60	8.18	2.56	4.57
Gabardine (B)	Afterchrome	6.41	3.74	4.99	3.12

Table 8: Tear strength results from piece-dyeing trial (a).

Fabric	Dyes	Tear strength (kg)			
		Control		Basolan AS	
		Warp	Weft	Warp	Weft
Crespino	1:2 Metal-complex	1.29	1.89	1.38	1.87
Sirofil	Milling	1.13	1.37	1.61	1.90
Sirofil	Afterchrome	1.08	1.37	1.50	1.76
Gabardine (A)	Milling	1.67	1.83	1.93	1.92
Gabardine (B)	Afterchrome	1.27	1.70	1.37	1.87

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8. The importance of colour fastness

Throughout the history of dyeing, the dyer has always been willing to pay more for products with better colour fastness, because his customers were willing to pay more for colour which would stay on the fibre and look the same many years afterwards as it did when originally purchased.

The modern dyer and consumer are no different. Both have an interest in the colour remaining on the fibres for the life of the textile concerned. Generally, the better the fastness properties, the greater the dyeing cost, both in respect to dyes and methods. A product with poor fastness will result in customer dissatisfaction, returns, and failure to repurchase brand names which show inadequate fastness properties.

Another reason for requiring good colour fastness is that when fibre is dyed at an early stage of processing it must be fast to subsequent wet processing and heat treatments that are experienced after weaving and knitting. In this case, the water and washing fastness properties which will eventually be required in the finished products will be gained as a result of the need for further processing after dyeing.

8.1   Fastness properties of textiles

(i)   Fastness to light

It is unlikely that the majority of textiles would avoid exposure to strong light for extended periods at some stage in their life. Automobile upholstery and window drapes experience continual exposure during daylight and must have very good fastness, whereas linings in clothes require little in the way of light fastness.

(ii)   Washing fastness

Garments which are frequently washed must not lose their colour in the washing process.

Dyes will have some tendency to move from the fibre back into solution unless the conditions are not sufficiently severe, or the dye has been linked to the fibre or changed in some way to prevent it moving off the fibre to any significant degree. Staining of other fibres present in the washings must also be evaluated. The more severe the washing test, the more likely dye is to be removed from the fibre.

(iii)   Water fastness

Similar remarks apply to those for washing fastness. Testing for fastness to chlorinated water and sea water must also be considered.

(iv)   Drycleaning fastness

Because some textiles are not suitable for washing, either because of their construction, fibre components, or perhaps even because of their low water or washing fastness, they must be drycleaned. This means that the colour must be fast to the usual dry cleaning solvents, not only so that the textile does not fade, but so that other textiles being cleaned in the same lot are not stained by the loose dye.

(v)   Perspiration fastness

Garments, particularly those worn next to or near the skin must have good perspiration fastness otherwise the fabric will experience local colour changes and stain adjacent fabrics – or bodies! Similar remarks apply to those in 'washing fastness' above, but more factors have to be taken into account. Perspiration contains significant quantities of

histidine, which can influence fastness, and can be either alkaline or acidic, which may also influence fastness, depending on the dyeing system used.

(vi) Chlorine fastness

The presence of chlorine producing agents in some washing formulations and in swimming pools requires garments and other textiles to be fast from chlorine, for example, towels and operating theatre clothes. The tests required are variants of the washing and water fastness tests.

(vii) Rubbing (crocking) fastness

It is necessary to test the degree of transfer of colour from one fabric to another under wet and dry condition. People tend to wear layers of clothing which rub against each other during movement, and also when pressed against objects by body weight when a person is seated.

8.2   Types of textile merchandise

(i) Fashion apparel

Fashion apparel, particularly women's fashion apparel, is the more relatively short lived, e.g. six months, type of garment. Its life is governed by the acceptability of its style rather than the ability of the garment or the fastness of its colours to survive for its wearing life. The garments are not as likely to be worn repeatedly as is, say, workwear.

(ii) Workwear

Workwear includes overalls, uniforms, dust coats and so on, which generally afford protection for, or alternatives to, everyday and fashion garments. They generally have higher fastness requirements than fashion apparel, and are expected to maintain shade and hence 'uniformity'. Wearing will be considerably longer than for fashion apparel garments.

(iii) Domestic textiles

Curtains and upholsteries are the principle domestic textiles.

(iv) Carpets

Carpets use many of the fibres of apparel and domestic textiles.

(v) Automotive upholstery

Particularly high fastness levels and durability are required for textiles used in this area. Extreme conditions are experienced by these fabrics in closed vehicles in direct sunlight.

(vi) and (vii) Swimwear and towelling

These textiles are both likely to experience exposure to agents not generally encountered, that is, sea water, and heavily chlorinated waters from swimming pools.

(viii) Hosiery

Hosiery has a need for good fastness because of its intimate contact with the body and body fluids. Hosiery includes men's, women's and children's socks, and panty hose, stockings, and their variants.

8.3 Fastness requirements for textile merchandise categories

(i) Fashion apparel

Dying should be fast to washing, water, and perspiration since these are conditions to which the garments are most likely to be exposed. For some delicate fabrics, dry cleaning fastness will be important if the garment is non-washable. Reasonable light fastness for the end use is obtained by most dyeing systems, although under Australian conditions this would have to be higher than for more temperate European conditions. Reasonable rub fastness is also necessary. Change of shade in a fashion garment, provided it is even, is not as critical as limited staining characteristics.

(ii) Workwear

Because of the more stringent criteria for performance and the need to maintain uniformity, workwear must be fast to washing, dry cleaning, perspiration, and rubbing. The severity of the washing test will be greater than that required for fashion apparel as repeated laundering is probable. Dry cleaning is also likely, particularly to remove oily stains on overalls and so on. Perspiration and rubbing fastness standards are also high because garments will be exposed to these conditions repeatedly. Uniforms worn outside must also have good light fastness.

(iii) Curtains and upholstery

Because of their exposure in windows, curtains need to have a high light fastness. This is not as critical with upholstery because it is not as likely to be exposed directly to light, but the light fastness should still be good. Curtains and upholstery are usually dry cleaned rather than washed, and hence dry cleaning fastness is to be stressed more than washing. The number of clearings in the life of these textiles is not likely to be high. Rubbing fastness of upholstery is important.

(iv) Carpets

Carpets need high light fastness, and rub fastness. Because steam cleaning is frequently applied to carpets, they must also be fast to steam.

(v) Automotive upholstery

Very high light fastness is essential, particularly under Australian conditions. Rubbing, water and perspiration fastness should also be excellent to withstand exposure during the life of the vehicle. The fabric must maintain its usable state for much longer than other textiles and under more severe conditions then they experience.

(vi) and (vii) Swimwear and towelling

Both categories are used outdoors and require good fastness to light and washing because of their exposure to chlorinated water and to light. Apart from their use as 'swimming' towels, domestic towelling will be washed frequently and requires good washing fastness for this reason.

(viii) Hosiery

Frequent washing requirements and exposure to perspiration and rubbing bring these fastness properties to the fore. The relatively short life of the garments, or their lack of exposure, makes light fastness unimportant. Shade stability is not as critical. The emphasis is on staining properties on other fibres rather than change of shade.

8.4   Development of test methods

Methods of colour fastness testing are developed by committees of scientists, technicians, and consumers.

The process of determining a suitable method takes a considerable amount of time, as it must be capable of being reproduced and have some relationship to the real life performance of the textile in regard to the property being tested. The methods are reviewed periodically to ensure that they maintain their relevance, and use the latest development in testing technology and assessment.

The test methods are published regularly in manuals such as the Society of Dyers and Colourists' *Standard Methods for the Determination of Colour Fastness of Textiles*, and the American Association of Textile Chemists and Colourists' *Technical Manual.* They are also published as national standards. Australia has such committees working under the auspices of the Standards Association. The methods briefly described in this unit are the most common ones. The methods should only be applied after reference to the appropriate manuals.

8.4.1   The grey scales

Most colour fastness tests require an assessment of the change in colour of the test specimen and an assessment of the degree of transfer of colour to other fabrics used in the test. Thus, the grey scales consist of two separate scales, one for each of the above types of assessment.

The grey scales have predetermined levels of contrast which provide testers with a numerical assessment of the test performed.

(a)   Grey scale for colour change

The scale consists of five pairs of standard grey chips, each pair representing a difference corresponding to a numerical fastness rating. The rating is done by comparing the difference in colour of the tested specimen and the original textile.

A.   The Grey Scale for Colour Change   (Show actual scale)

B.   Part of the Grey Scale for Staining   (Show actual scale)

The chips of the pair representing Rating 5 are identical. Each of the other ratings has an identical chip to those in Rating 5 and a lighter chip. The difference in depth of a pair of chips for a given rating is set as a standard number of colour difference units. The ratings have the following interpretation:

5.   negligible or no change

4.   slightly changed

3.   noticeably changed

2.   considerably changed

1.   much changed.

Half steps are also used, for example, 4–5, 3–4, 2–3, 1–2. If a tone shift occurs on testing the direction of the shift can be described using the following terms:

Br   Brighter

Bl   Bluer

D   Duller

G   Greener

R   Redder

S   Stronger

W   Weaker

y   Yellower

Thus, a shade change may be described as: 3–4, weaker, yellower, that is, it has a contrast change between 3 and 4, and is weaker and yellower.

(b)   Grey scale for staining

The grey scale for assessing staining is constructed in the reverse manner to that for assessing colour change. In this case, Rating 5 is represented by two identical white chips, and the progressively lower ratings by one of these white chips and a darker one.

Assessment is made by comparing the difference in colour of the stained and unstained cloth with the differences on the scale.

The ratings have the following significance:-

5   Excellent

4   Good

3   Fair

2   Poor

1   Very poor

Intermediate ratings are also used.

8.4.2   Light fastness testing

In testing light fastness, a specimen from the textile being tested and the standards are exposed to a light source under set conditions for a sufficient time to produce set amounts of colour change.

The standards are a series of blue dyeings on wool, graded so that each higher numbered sample is approximately twice the fastness of the preceding standard. They are frequently referred to as Blue Scales.

Up to nine standards can be used, graded as follows:

9   Superlative

8   Outstanding

7   Excellent

6   Very good

5   Good

4   Fairly good

3   Fair.

2 Poor

1 Very poor.

Intermediate ratings are also possible.

Strips of the blue standards, together with the test specimens, are arranged on a card and partly covered with an opaque strip so that unexposed sections can later be compared.

Two approaches to evaluation exist: the single-stage method and the two-stage method.

(i) The single-stage method

The standards and samples are exposed until a 'just perceptible difference' is reached between the covered and exposed areas of the samples. This is a change visually equal to standard 4 on the grey scale. The colour change of the blue standard is then examined and compared to the sample. The number of the blue standard which has just faded to the same extent as the test specimen is quoted as the light fastness rating. As indicated, intermediate ratings are possible.

(ii) The two-stage method

This method is set out in the *Australian Standard AS2001. 4-21-1979: Determination of Colour Fastness to Light Using an Artificial Light Source*. In this method, test specimens are again half covered with an opaque strip and exposed to light. As irradiation proceeds, observations are made of the appearance of the test specimens and of the standards. When a change in colour of the test specimen can just be perceived, the number of the standard just showing a perceptible colour change is recorded. This value is referred to as the 'preliminary assessment'.

Exposure is then continued until blue standard 7 shows a change in colour equal to standard 4 on the grey scale. The change in colour of the blue standards and the number of the blue standard showing a similar change to that of the best specimen is recorded. This value is referred to as the 'final assessment'.

The light fastness rating then is given by the final assessment followed by the preliminary assessment in parentheses; for example, 4 (3) where 4 = final assessment; 3 = preliminary assessment.

If the final and preliminary assessments are the same, one number only is given.

8.4.3 Exposure methods

Exposure can be to daylight or artificial light sources. For daylight exposure, the samples are placed in a glass faced cabinet facing the equator, and sloping at an angle from the horizontal approximately equal to the latitude of the location at which the tests are made. Shadows should not fall on the case. The specimens and standards remain in the cabinet 24 hours a day, and are only removed for inspection.

Inspection is required at intervals to check the degrees of fading. For example, when blue standard 2 reaches a shade change of 4, it and any specimens which have reached that level of change are removed and the remainder re-exposed. The process continues until all samples change to 4. In the case of the two-stage method, successive opaque strips are placed on the cards as different levels of change are reached.

Exposure to artificial light sources includes Xenon-Arc lamps, Carbon-Arc lamps, and more recently, the much cheaper Mercury Vapour lamps. Exposure under these conditions will not necessarily be identical to daylight exposure, but is generally used as a good guide. The methods have the advantage of relative speed compared to daylight, particularly in

winter. Manufacturers' pattern cards for dyes will generally list both daylight and artificial fastness ratings. Daylight ratings are usually higher, and accepted as the most realistic.

Assessment conditions

After exposure, samples and standards should be kept in the dark for two hours at room temperature to cool off and regain moisture from the atmosphere. Assessment should be done with adequate illumination from an appropriate angle.

8.4.4 Washing fastness

5 cm x 5 cm test samples have pieces of white fabric sewn to them along all four edges and are laundered in a detergent solution in glass or metal cylinders, which may or may not contain steel balls. The white fabric will be cotton, wool, acetate, nylon or a specially manufactured multi-fibre cloth.

Laundering conditions vary both in time and temperature, and the conditions used should be specified when describing ratings. The Australian Standard for colour fastness to washing, A52001.4.15, describes seven procedures ranging from conditions of simulated hand laundering to prolonged, very severe conditions of machine laundering. A special machine called a laundrometer is used to agitate the samples and control the temperature and time of the washing. After washing is complete, samples are rinsed and dried in air at no more than 60°C.

Assessment of colour change of the original and washed specimens, and of the degree of staining, is done using appropriate grey scales.

8.4.5 Water fastness

Specimens are prepared with white fabrics attached as in the washing test. They are then immersed in distilled water before being placed between glass plates and held under specified conditions of time, temperature and pressure, for example, 40°C + 2°C for four hours under a five kilogram pressure. See Appendix B.

The specimens are then removed and rinsed and allowed to air dry at room temperature. Colour change and staining are then assessed using the appropriate grey scales.

The water used may be sea water or chlorinated water for testing of colourfastness to these agents.

8.4.6 Drycleaning fastness

The method set out in *Australian Standard A52001.4.16: Determination of Colourfastness to Drycleaning Solvents* is as follows.

A specimen of the textile to be tested is sewn to an appropriate undyed cloth of the same size and placed in a stainless steel container together with 20 stainless steel balls and 200 ml of solvent. The container is then placed in the laundrometer and agitated for 30 minutes at 30° ± 2°C. The test specimen is then removed, rinsed in fresh solvent and the excess solvent removed using absorbent cloth, paper or by centrifuging.

The sample is then dried in air at 55° ± 5°C and assessment of the degree of colour change and staining is done using the appropriate grey scales. The solvents used in this test are white spirit and perchloroethylene, and two tests should be done to assess colourfastness to each of these solvents.

8.4.7 Perspiration fastness

The method is the same as that used for water fastness. In fact, the apparatus used to hold the specimens between glass under pressure is known as a perspiration tester.

Two specimens need to be prepared with white fabrics adjacent, as in the washing test. One is wet out in an acid perspiration solution and the other is an alkaline perspiration solution. The solutions contain sodium chloride-histidene monochoride, disodium hydrogen phosphate and sodium dihydrogen phosphate.

Treatment for at least six hours at 40°C ± 2°C is required. The specimens are then removed, air dried and evaluated using the appropriate grey scales for colour change and staining.

8.4.8 Chlorine fastness

Methods already described are used to test for chlorine fastness. Fastness to chlorinated water uses the water fastness method. Fastness to chlorinated washing conditions uses the washing fastness method.

Australian Standard AS2001.4.5: Determination of Colourfastness to Chlorinated Swimming Pool Water, gives a method of testing textiles for this type of colourfastness. The method uses a solution employing a phosphate buffer to provide a pH of 7 ± 0.2 and containing 25 mg of available chlorine per litre. See Appendix A.

The test specimens are prepared as before and treated in containers in the laundrometer for 60 minutes at 25°C ± 20°C. The specimens are then rinsed, dried and assessed as before.

8.4.9 Rubbing fastness

Rubbing or cracking fastness measures the amount of colour transferred to wet or dry white test cloth under standardized rubbing conditions.

A machine known as the American Association of Textile Chemists and Colourists (AATCC) crockmeter is used. The test specimen is placed on the base of the crockmeter and a five centimetre square of white fabric clipped over the end of a protruding finger on the weighted sliding arm. The arm is lowered to place the finger in contact with the specimen and the machine cranked 10 times, giving a total of 20 passes across the fabric. The white square is then removed and evaluated using the grey scale for staining.

The wet test is done by wetting out the white square in distilled water, expressing moisture out until it is approximately 65% of the weight of the fabric and testing as above. The sample is air dried before evaluation.

Wet cracking is generally rated lower than dry cracking. A rotary vertical crockmeter is also used which rotates the finger against the specimen, rather than stroking it.

9. Principles of different dyeing machines

Wool may be dyed using a number of different types of dyeing machines and in numerous forms from loose fibre to woven and knitted fabric or even garments.

The stage in the manufacturing process at which dyeing is carried out is dependent on a number of factors, and some of these will be discussed below.

As a rule it is preferable to carry out the dyeing operation as late in the manufacturing chain as possible as this leads to just in time deliveries and reduced stock holding. However, there are good reasons why this is not always desirable or possible.

9.1 Loose stock dyeing

Wool is often dyed in fibre form. This of course means that the dyeing is done at the earliest stage of processing and colouration commitments must be made well in advance of the finished product.

Loose stock dyeing is most often used these days as a precolouration method in the production of woollen spun yarns in the carpet manufacturing industry where large lots of up to 12 tonnes per colour are produced.

The main machine designs are:

* conical pan machines

* atmospheric radial flow machines

* pressurised radial flow machines.

9.1.1 Advantages of loose stock dyeing

(a)   It is possible to dye very large lots of up to 12–14 tonnes per colour. This is done by dyeing numerous batches of perhaps 500 kilograms each and then blending all of these batches together.

(b)   This method is ideal for instance when supplying carpet to large commercial installations such as hotels where many thousands of metres of the same colour may be required.

(c)   This dyeing method provides the ability to even out any colour irregularities within the individual dye batches during subsequent blending.

(d)   It provides a simple way of dyeing blends of different fibres as the optimum dyeing procedure may be employed for each of the individual fibres.

(e)   By this method it is possible to mix different colours together to produce heather mixtures.

Disadvantages of loose stock dyeing

(a)   Economy of scale is lost if small lots are dyed.

(b)   Very long lead times are required between time of dyeing and production of finished product.
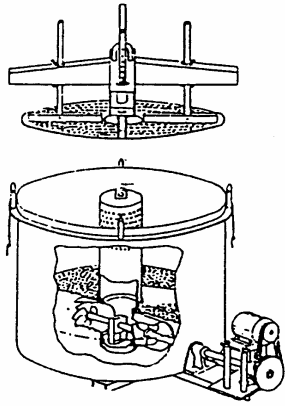
Radial flow loose stock dyeing machine.
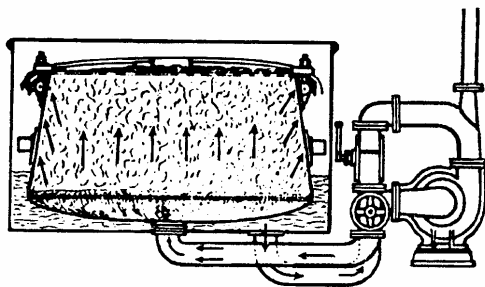
Conical pan loose stock dyeing machine.
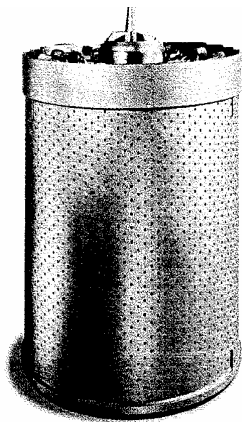
Loose stock carrier for pressure dyeing machine.

9.2   Top dyeing

Wool is often dyed in top form. Wool tops are produced after combing, which is a preparatory stage before worsted spinning. The tops are actually balls of sliver that weigh anywhere between three and 10 kilograms, or are more commonly made into bump tops of up to 20 kilograms.

Modern top dyeing machines are multipurpose machines, which may be used for dyeing yarn on packages and also loose fibre. They are able to dye at high temperatures under pressure so may be used for dyeing fibres other than wool.

Advantages of top dyeing

Top dyeing shares similar advantages to loose stock dyeing and is the first opportunity to dye the fibre in the worsted spinning production chain.

Disadvantages of top dyeing

As with loose stock dyeing, the economies of scale are lost if small lots are required. Once wool tops have been dyed, they then need to be recombed prior to spinning, which adds an additional cost.
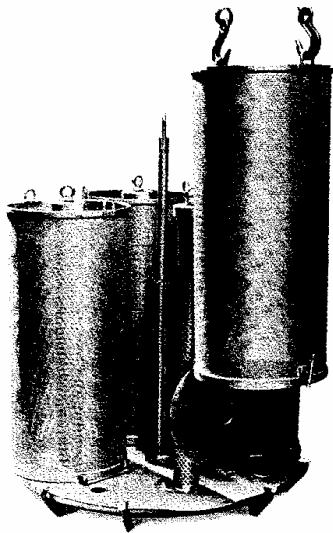
Top carrier for pressure dyeing machine.

9.3   Yarn dyeing

Dyeing is often carried out in yarn form for a number of reasons. For colour woven fabrics such as checks and fancy designs, and also for multicoloured knitted garments, the requirements for some individual colours may be very small and there may be a large number of colours in the design. In this situation it is not practical or cost-effective to dye large lots of tops for each colour. Yarn can be dyed in lots of from one kilogram to 500 kilograms or 1000 kilograms, depending on the size of the machines available.

Package dyeing

Package dyeing is now a very widely used technique for producing coloured yarn for colour woven fabrics and knit goods. Modern package dyeing machines have a high degree of versatility with regard to batch sizes and the fibres which may be dyed.

The machines may be operated under pressurised conditions at temperatures up to 140°C making it possible to dye fibres such as polyester. The yarn to be dyed is wound onto perforated dye centres which may be disposable plastic or stainless steel springs, which are reused. The packages may be in the form of cones, cheeses, muffs or bobbins.

The packages are loaded onto a carrier with perforated spindles and are normally compressed by about 30% to reduce the possibility of channelling and leakage between packages.

These machines have very efficient pumping systems with the facility to reverse the flow direction and can dye at liquor ratios down to 1:6.

A general rule of thumb for flow rates is that 30 litres per kilogram of yarn per minute is about optimum.

Advantages of package dyeing

(a)   Reduced lead times from order to finished product – reduced stock holding.

(b)   Extremely versatile in batch sizes – any size lot from one kilogram to 1000 kilograms, depending on machinery available.

(c)   Yarn packages may be assembled on two-for-one twisters thereby saving a winding operation.

(d)   Improved spinning yields as fibre is not damaged prior to spinning.

Disadvantages of package dyeing

(a)   Loss of yarn bulk if special dyeing methods are not used.

(b)   Yarn flattening on inside of package.
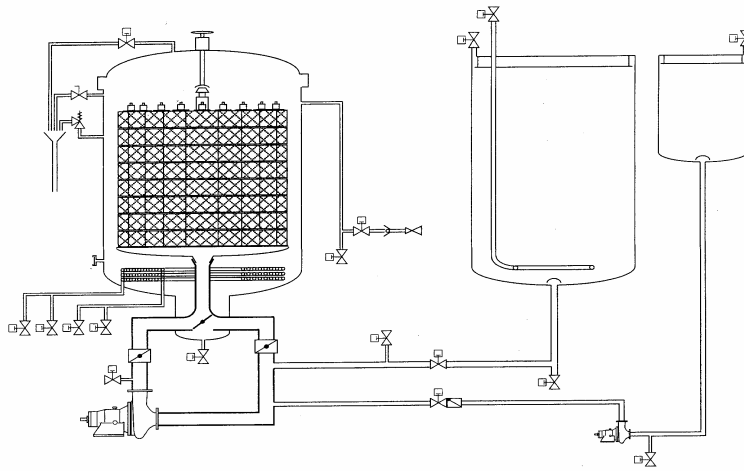
Schematic of pressure package dyeing machine.
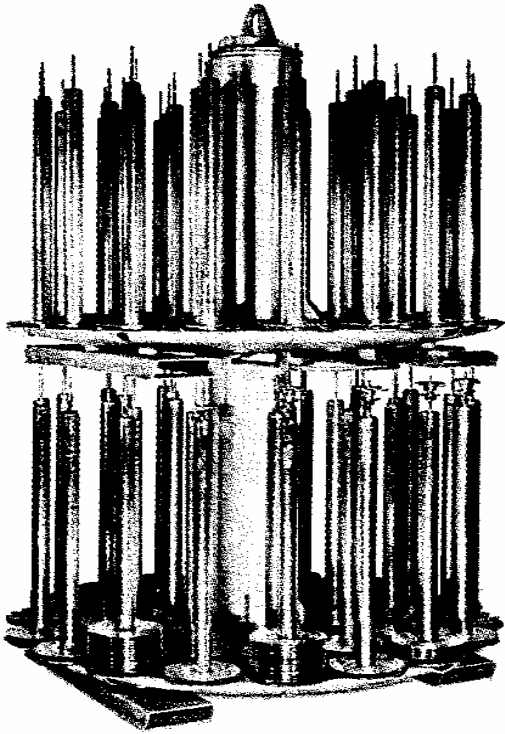
Yarn package carrier for pressure dyeing machine.
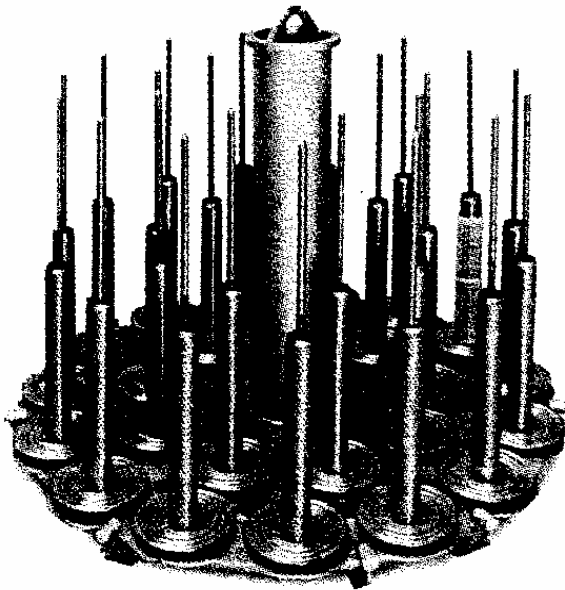
Yarn package carrier showing flexible spindle height.

Hank dyeing

The tradition method of dyeing yarn is to do it in hank form. It is carried out in machines with fairly gentle liquor flow so as to reduce channelling. The hanks of yarn are supported by sticks (steel rods) at the top and bottom of the machine to cater for reversal of the liquor flow direction.

Advantages of hank dyeing

(a)   Low liquor flow rates and very little tension on the yarn provide a very gentle action during the dyeing cycle and maintain the yarn bulk or loftiness.

(b)   Improved spinning yields.

(c)   Reduced lead times and inventories.

(d)   Ideal dyeing system for wool and acrylic yarn which is easily deformed during dyeing.

Disadvantages of hank dyeing

(a)   Little flexibility in batch sizes as machines must be fully loaded

(b)   Hanking and backwinding operations add extra cost.

(c)   Loading material carriers is slow and labour intensive.
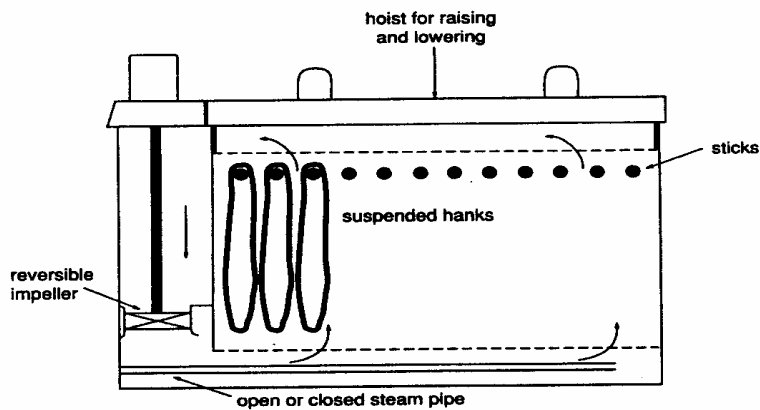
Schematic of hank dyeing machine.
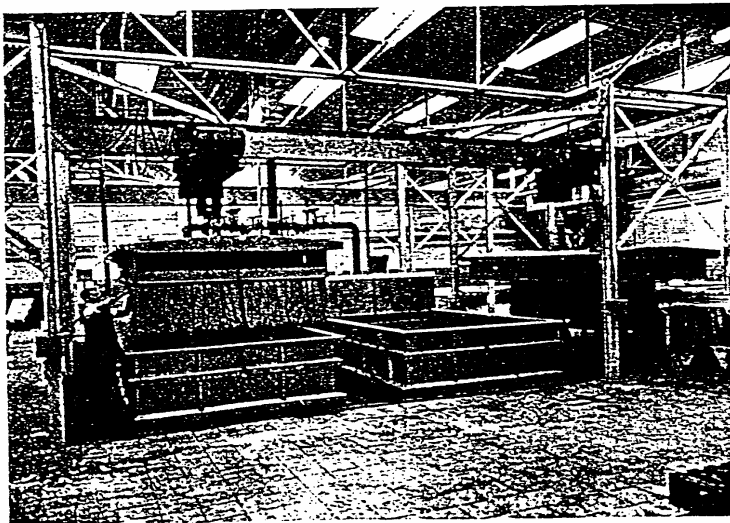
Atmospheric hank dyeing machine.
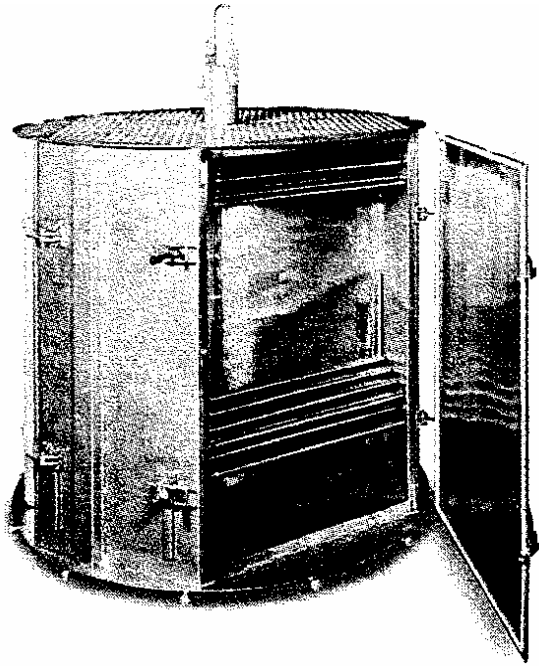
Hank carrier for pressure dyeing machine.

9.4 Fabric dyeing

Fabric is dyed using a number of different types of machines including winches, beam dyeing machines, jigs and jet dyeing machines.

For wool fabrics which are produced from woollen spun yarns, winches are often preferred as they can have a positive effect on fabric consolidation. However, for wool and wool blend fabrics produced on the worsted system, soft action jet dyeing machines are usually preferred.

In special cases with wool fabric, which is very delicate or prone to creasing, it is sometimes necessary to dye them on a beam dyeing machine.

Advantages of fabric dyeing

(a)   Very short lead times and minimum stockholding of finished goods.

(b)   Amounts exactly matching the size of the order may be dyed.

(c)   Leads to highly efficient processing as only white fabric needs to be woven or knitted.

Disadvantages of fabric dyeing

(a)   Restricted colouration flexibility as only solid colours can be dyed unless blends of different fibres are used

(b)   A certain amount of permanent set may be imparted to the fabric which may prove undesirable in later finishing operations.
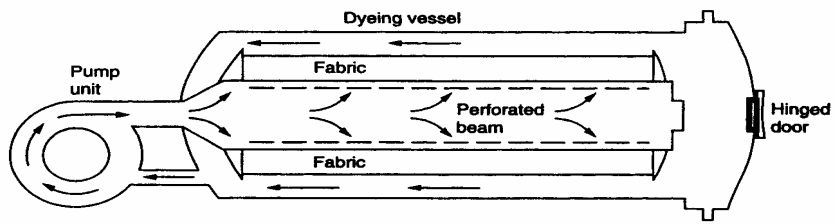
Figure 5.7 High temperature beam dyeing machine.
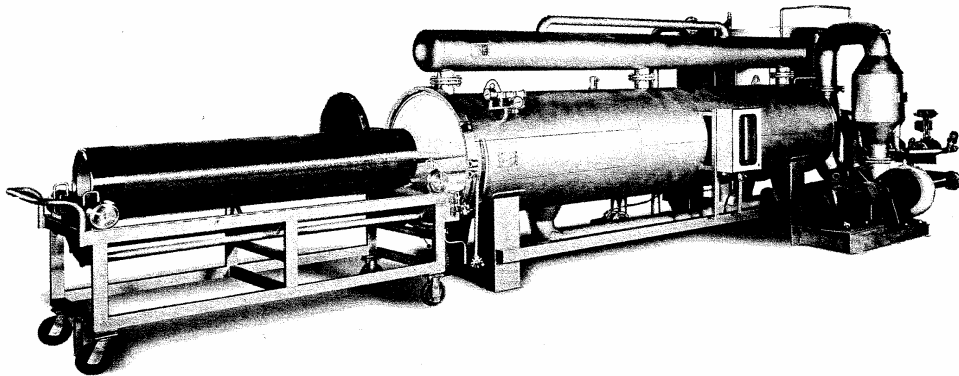
Modern beam dyeing machine.
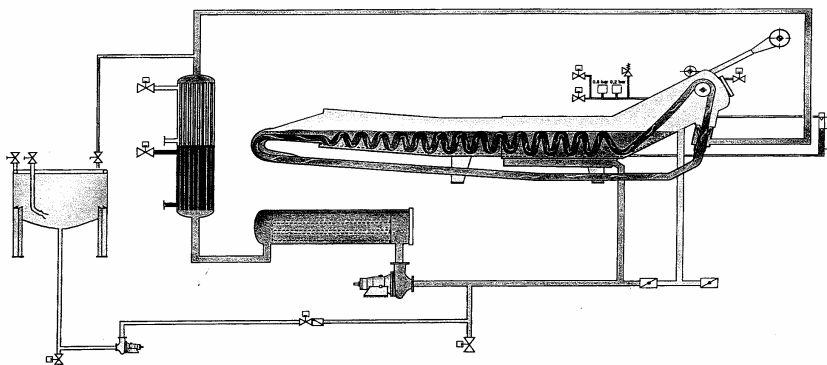
Schematic of a jet dyeing machine.
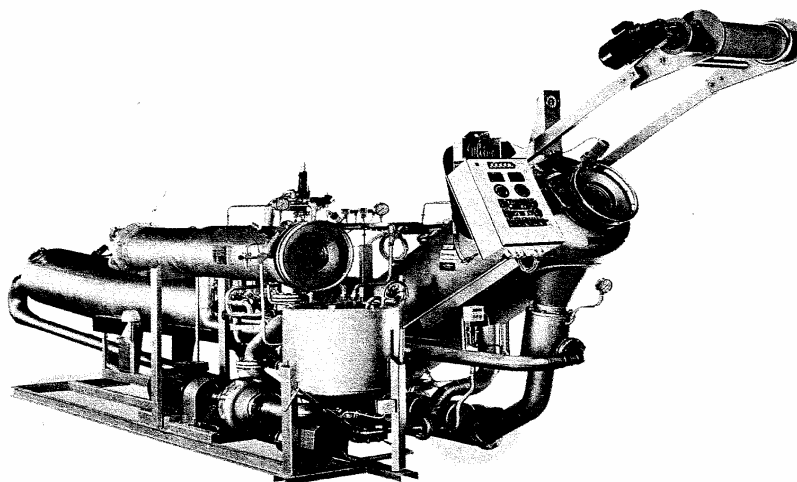
Modern Softflow jet dyeing machine.

9.5   Garment dyeing

Garment dyeing machines have long been used for dyeing socks, stockings and pantyhose and are sometimes used for dyeing fully fashioned knitted garments.

There are a number of different types of machines from rotary drum machines to side and overhead paddles and the more modern front-loading rotary drum garment dyeing machines. The front-loading rotary drum machines have the advantage that they are also used for extracting water from the dyed goods.

Garment dyeing is not widely used for dyeing wool or wool blend products except for shrink-resisttreated fully fashioned knitted garments or socks.

10. Colour perception and measurement

With most textiles intended for the apparel market the attention of the purchaser is first engaged by their aesthetic appeal, and at that occasion colour is often the most important factor.

At the end of the dyeing cycle a decision will have to be made as to whether the dyeing has been successful in achieving a matching to the customer's required shade. The problem, which has long been realised, is that human perception of colour is a physiological sensation that defies a concise verbal definition. It is not entirely certain if any two people will see a coloured object exactly the same way. Most people would recognise and describe a red coloured pen as red. The sensation of the colour red is interpreted by our eyes and brain, while we have learnt o describe this particular sensation as red. Do we know that the same coloured object produces the same response in different people? Colour matching experiments carried out with trained industrial colour matchers indicated that different responses are obtained, even if those responses were within narrow limits.

Genetics and age both contribute to how the eye sees colour and are an explanation for the differences in colour perception. People can still communicate about colour because just over 95 per cent of human beings have a very similar response to colour stimulus. A general common description of the colour red could use the terms *crimson*, *scarlet*, *rose*, *strawberry*, *claret* and so on, to try and describe red by reference to other objects. Adjectives such as *bright*, *dull* and *deep* make colour expression more precise but are still subjective.

A methodical approach to the verbal assessment was originally the only means for transmitting opinions about the appearance of colour. However, these verbal expressions are subjective in their nature and vague in defining colour exactly. Many attempts have been made in the past to overcome the deficiencies of subjective colour description by describing colour objectively.

10.1 Nature of light

For a colour to be perceived light must be present, for the absence of light means that a colour detector, such as the human eye, will not be able to function.

A clear definition of the nature of white light has proved very elusive, but it is known that light is a form of electromagnetic radiation and that visible light is only a small portion of the overall electromagnetic radiation spectrum.

10.2 The visible spectrum

When daylight passes through a prism it is separated into a spectrum of seven colours: violet, blue, cyan, green, yellow, orange and red. This is known as the visible spectrum.

If the seven colours can be re-combined again they will produce white light. This can be done by passing them through an inverted prism.

Daylight (or white light) is a form of electromagnetic radiation that begins in the sun and travels outward through space as waves of energy. The distance between one wave and the next (the wavelength), varies greatly and results in many different forms of natural radiation. The **electromagnetic spectrum** covers wavelengths from cosmic rays to radio waves. Within this spectrum the only visible radiation is that which we see as visible light.
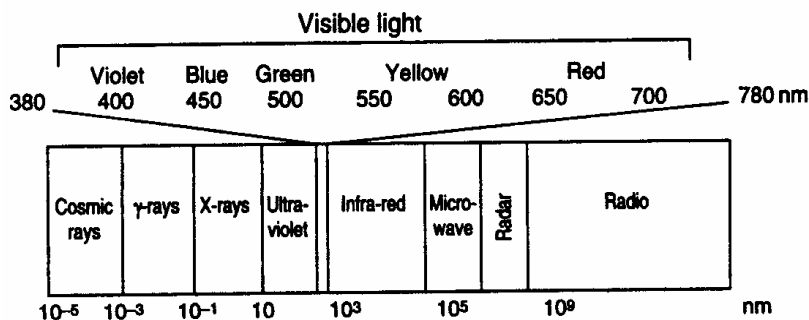
Electromagnetic spectrum.

The visible spectrum can be seen to be a very small portion of the electromagnetic spectrum, covering about one three thousandth of a millimetre.

Each colour within the visible spectrum has a different wavelength. Wavelengths are measured in **nanometres** (nm). A nanometre is one millionth of a millimetre. The wavelengths of the visible spectrum range from 380 to 700 nm. There is no definite partition between each colour, each one gradually changing from its neighbour across the spectrum.

When light of a particular wavelength in the visible spectrum reaches our eye it produces a unique effect. We describe this sensation as colour. This effect is caused by the wavelength stimulating the retina in the eye. The regions outside the visible spectrum cannot be seen by the human eye. Immediately below the visible spectrum is ultraviolet radiation (shorter wavelengths whilst immediately above the visible spectrum is infrared longer wavelengths).

Our eyes detect colour of an object by the wavelengths that are reflected from it. The established reasoning is that perceived colours are a property of the object with which they are associated, rather than a physiological sensation originating in the retina and interpreted by the brain.

An apple appears red because it reflects the red waves in the visible spectrum. The shorter wavelengths are nearly all absorbed by the apple.

The physical and chemical characteristics of an object determine which light is reflected from the surface and which is absorbed by it.

Absorbed wavelength (nm)	Hue of absorbed light	Perceived hue
400–440	Violet	Greenish-yellow
440–480	Blue	Yellow
480–510	Blue-green	Orange
510–540	Green	Red
540–570	Yellow-green	Purple
570–580	Yellow	Blue
580–610	Orange	Greenish-blue
610–700	Red	Blue-green

Relationship between wavelength and absorbed light and hue.

For a colour to be interpreted, three separate components must interact:

- a light source (for example, daylight)

Contemporary wool dyeing and finishing
Dyeing methods for wool: Arthur Fisher

- an object that can reflect wavelengths

- an observer which can receive the wavelength energy (for example, an eye).

If any of these components are altered, a change in the interpreted colour is likely. You will have seen how the colour of an object can appear to change in different light sources; under a fluorescent light an object can look very different compared to its appearance in daylight.

Colour detectors receive energy and recognise colour. The eye is not the only type of observer that can detect and interpret colour. There are a variety of instruments such as colourimetres and spectrophotometers that can detect and measure colour.

10.3 How the eye sees colour

The simplest and most commonly accepted theory on how colour is perceived by the human eye and brain is the Young-Helmholtz theory. The combined ideas of both Young and Helmholtz are known as the **Trichromatic theory**. According to this theory the eye contains three types of photoreceptors known as cones. Each cone is sensitive to a different part of the spectrum.

- One type of cone is very sensitive to red light, slightly sensitive to green and not sensitive to blue.

- One type of cone is very sensitive to green, slightly sensitive to blue but not sensitive to red.

- One type of cone is very sensitive to blue, slightly sensitive to green and not at all sensitive to red.
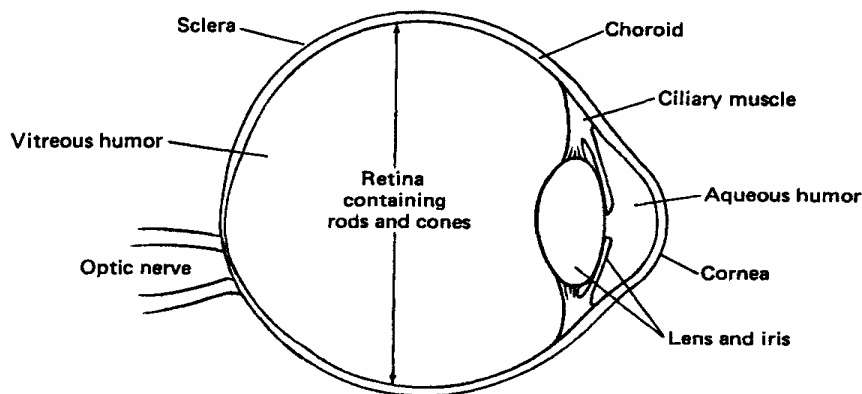
Anatomy of the eye.
The surface of the retina is covered with rods and cones. It is with the cones that we see light.

If pure light falls on the retina, the cone that is sensitive to red undergoes a chemical transformation, but the other two cones are unaffected. The chemical reaction sends a nerve signal to the brain, which is then interpreted by the brain. This is the perception of the colour red.
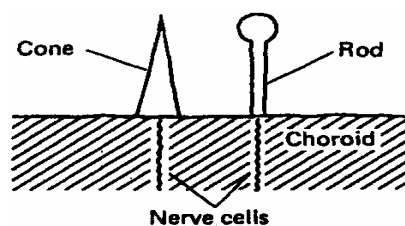
The structure of the retina surface. Cones are sensitive to light and see colour. Rods are sensitive to low light.

When white light, that is, light containing equal amounts of all the wavelengths of the visible spectrum, enters the eye all three types of cones are stimulated and we perceive 'white' or the absence of colour.

We see colours other than red, green and blue when the brain receives mixed signals. If the red and green sensitive cones are triggered, the brain receives the message of yellow, which can be either of an orange or greenish tint depending on the ratio of red to green receptors triggered. Green and blue receptors trigger to give cyan (light blue), again the overall colour varying with the ratio of the two receptors.

S. Short wavelength
M. Medium wavelength
L. Long wavelength
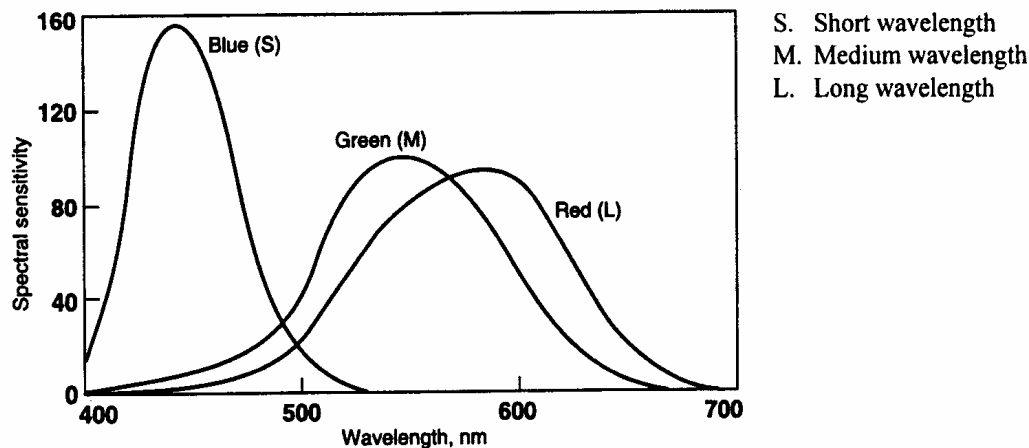
Cone sensitivity.

10.4 Colour deficiency

Not all people have perfect colour vision. Colour vision depends on effective colour receptors. If a person's retina lacks effective receptors for one of the primary colours, they will have difficulty in recognising all of the colours in the spectrum. Some people have no receptors in the eye and will view the world as if seeing a black and white television screen. This condition is extremely rare. The most common type of colour deficiency is confusion in the red–green area, with people unable to distinguish the two colours. About eight per cent of males, but only 0.5 per cent of females show some form of colour deficiency

10.5 Additive and subtractive primaries

Red, green and blue are called the additive primaries. This term comes from the fact that these three colours can be added together in different combinations to give any other colour. Light of these three colours, when mixed in the correct proportions, will give white. The additive primaries can not themselves be formed from other colours.

Colour television is an example of the **additive colour system**. The colour television screen contains substances called phosphors. On stimulation, one type of phosphor glows red, another green and a third blue. The television image is composed of tiny dots of these phosphors which will give the three colours of light, the brain doing the rest.

When two of these three primaries overlap the result is:

* magenta (a purplish red), from red and blue

* cyan (a greenish blue), from green and blue

* yellow from red and green.

Where red, green and blue overlap the result is white light because these colours cover all wavelengths in the spectrum.

Magenta, cyan and yellow are called subtractive primaries because they are each made by subtracting one of the three main primaries from the spectrum. They are made when white light falls on an object and one of the three main primaries is absorbed or 'subtracted'. Cyan is the result when red is subtracted from white; magenta is the result when green is subtracted and yellow is the result when blue is subtracted.

Where only two subtractive primaries overlap (the third is absorbed), they produce one of the secondary subtractives, which are the additive primaries. Where the three subtractive primaries overlap, black is produced.

Subtractive colour mixing is the most common way of producing colour. This is the basis of pigments and dyes used in colouration for printing and dyeing. For example, for a textile to appear red (in a white light), the dyes or pigments used will reflect both yellow and magenta and absorb cyan.

10.6 Colour constancy and metamerism

The human eye under certain lighting conditions will have difficulty in detecting particular colours. An example of this is a garment presented for sale in a retail outlet under fluorescent lighting, which may appear somewhat different in colour when viewed in daylight or in a room that is illuminated by an incandescent (tungsten) globe. The problem may be exacerbated if different pieces of the garment, for example, collars, cuffs or pockets, are cut from different rolls of fabric that have been dyed with different dyes. In this case different parts of the garment may look different when the garment is viewed in different light sources.

In both examples listed above, the problem is related to a change in spectral energy distribution of the light reflected back to the eye from the garment in moving from one light source to another.

The first example is referred to as **colour constancy**, while the second is referred to as **metamerism**.

Colour constancy refers to the ability of a coloured article to give the same general colour impression under different light sources irrespective of the dyes used. Metamerism, by comparison, refers to a change in the appearance of two coloured textiles dyed with different dyes that have been matched under one light source, when they are viewed under a different light source.

In dyeing, a non-metameric match will always be achieved if the dyes which are used to dye textiles are kept constant. The problem may arise where a company sources material from different suppliers or there is a change to the dye recipe.

The same shade matched on different fibres may also be a problem; for example, where an acid dye is used to dye wool or nylon and needs to match polyester, which must be dyed with disperse dyes. The two dyes from different dye classes may show different reflectance under different light sources. In this case metamerism or colour constancy will have to be controlled by careful dye selection.

10.7 Communicating about colour

The subjective nature of describing colour means that there are inherent problems within the industrial applications in colour matching.

When does a production batch match a standard?

If a shade does not match, when does it fall within tolerable amounts of the master standard and when does it not?

Obviously, a close rapport between the dyer and the customer is required. However, if a colour matching assessment can be made objectively, an independent 'pass' or 'fail' judgement can be achieved.

Many attempts have been made to objectively define colour. One of the most important is the **Munsell system**.

10.8 The Munsell system

In 1905, the American artist A.H. Munsell developed a system for expressing colour that utilised a great number of paper chips. The chips were used for a visual comparison with a colour sample. Each chip in the Munsell system has a notation so a colour could be referred back to the Munsell system. The Munsell system acts as a big colour atlas or catalogue of colours.

The significant breakthrough with the Munsell system over all previous colour perception theories is that Munsell defined colour within a three-dimensional space. In this system colour is notated in terms of:

- hue

- value

- chroma.

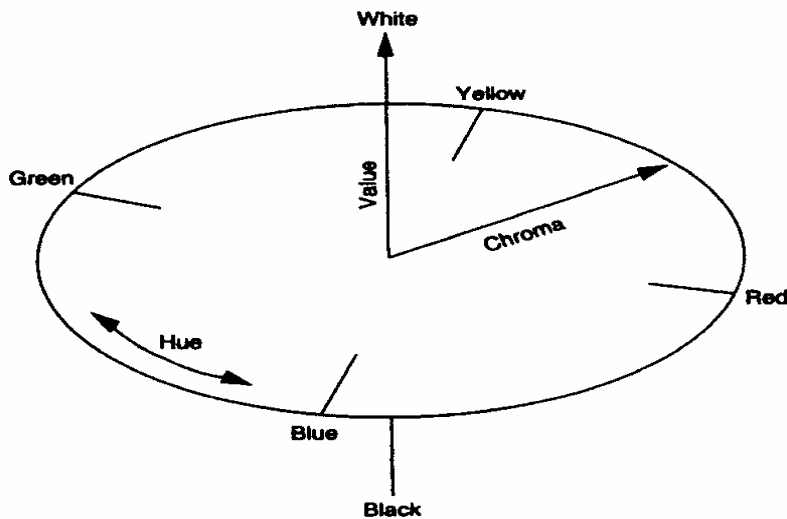Hue describes colour in terms of red, green, blue, yellow and so on.

Value describes lightness or darkness, in that value increases to white at the top end of the central vertical axis and decreases in 10 steps to black at the bottom. Value scales neutral greys from white to black.

Chroma describes the vividness or intensity of a colour. It is a description of a colour's purity (or lack of greyness), and increases outwards from the central vertical axis.

Although the concepts of the Munsell system have been refined into more modern theories, the ideas of hue, value and chroma are still relied upon as originally developed by Munsell.

One disadvantage of applying the Munsell system to textiles is that paper chips were used. Differences inherent in the reflectance of paper compared to textiles means that some of the brightest colours are difficult to achieve.

The Munsell system does provide an objective method of describing colour, but the level of precision it provides is still inadequate for denoting the colour of a dyed textile.

The Munsell colour shield.

Munsell co-ordinates and hue qualifiers.

10.9 The CIELAB system

Ultimately, precision can only be attained with a system using continuously variable co-ordinates rather than stepwise scales.

The Commission International de l'Eclairage (CIE International Commission on Illumination) has put forward a system for the objective measurement of colour with reference to a revised concept of colour space.

There have been many efforts to develop a more suitable scale for colour co-ordinates than the Munsell system, and it is now possible to obtain a precise objective assessment of the extent to which production, or laboratory trial dyeings differ from the required shade through instrumental matchings.

The CIELAB system of colour space can best be understood as a three-dimensional cylinder.

Colours are described by means of:

- L = lightness (or value)

- C = chroma

- H = hue.

It is also possible to describe any colour's site within this three-dimensional cylinder by means of numerical values L, A and B in a grid system of co-ordinates.
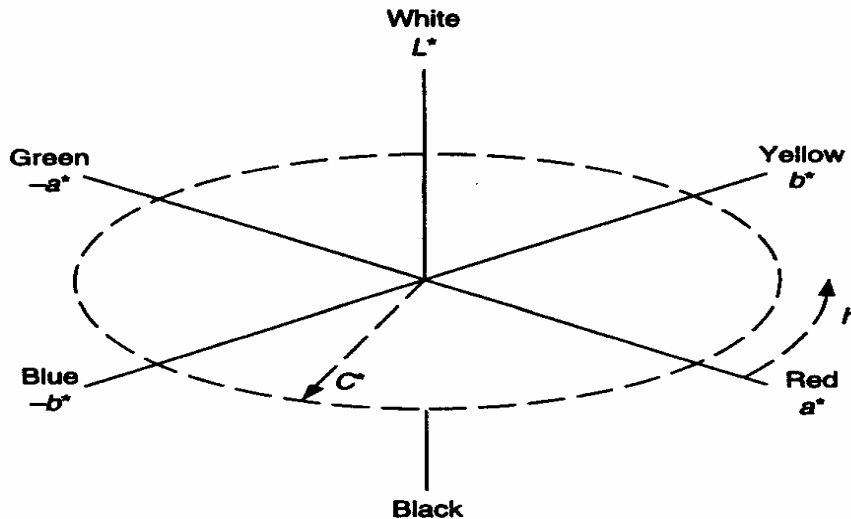
CIELAB colour space.

The CIE system takes the three components that comprise **the colourimetric equation**, namely:

- a light source

- an object which can reflect light

- an observer that can detect the reflected wavelengths.

Each of these three components can have a mathematical value assigned to it:

- The light source can have a numerical value assigned to its power distribution across the spectrum.

- An object can have a numerical value assigned to its reflectance across the spectrum.

- Numerical values have been assigned by the CIE for what is described as the Standard Observer.

The fact that a numerical value can be obtained for each component of the colourimetric equation means this data can be processed by computers to achieve an objective assessment of colour.

This is a clear advantage and the replacement of verbal descriptions by unambiguous measurements has led to significant improvements with which colours can be selected and matched to a customer's request.

Subsequent commercial dyeings can be compared with a master standard, and a mathematical difference indicating the variation in three dimensional colour space can be described. A tolerance value accommodating lightness, value and hue can then be set so that subsequent batches can be judged 'pass' or 'fail' in relation to the master standard.

10.10 Instrumental match prediction

Computers can be used to provide accurate colour matching systems. They are based on measurements between 380 nm and 700 nm with total accuracy, relying on the reaction to the wavelength produced.

This facility together with the colour response of a large range of dyestuffs will give a formula for any sample requested. It is usual for dyestuff companies to include all of their dyestuffs in the system. Upon presentation of a sample, they offer the customer a range of formulae. This range gives the exact shade with variations in fastness and cost.

When attached to computers, a large range of functions are offered including recipe bulking, shade quality control, production shade additions, recipe correction, shade sorting of rolls of fabric and inventory control of dyes and chemicals.

11. Acknowledgements

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