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Chemical analysis of textile coatings and membranes

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7.1   Introduction

Coated and laminated textiles usually consist of a textile substrate, which will typically be a woven, knitted or nonwoven fabric, combined with a thin, flexible film composed of a natural or synthetic polymeric substance. A coated fabric is one in which the textile substrate has a polymer film applied directly to one or both surfaces as a viscous liquid in a solvent or water, the thickness of which is controlled by application via a blade or similar aperture. A transfer coated fabric is an intermediate product in which a thermoplastic film is first prepared on a release paper prior to thermally bonding to the textile substrate. A laminated fabric usually consists of one or more textile substrates that are combined with a pre-prepared polymer film or membrane by adhesives or heat and pressure (Hall, 2000).

7.2   Chemical types used in coatings and membranes

A wide range of polymers which form thin, flexible films are used. They can be split into two categories, polymeric elastomers and rubbers. The polymers include polyurethanes, polyvinyl chloride, polyvinylidene chloride, polyethylene, polytetrafluoroethylene, silicone elastomers, polyacrylates, and chlorinated and chlorosulphonated polyethylenes.
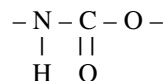
7.2.1   Polyurethanes (PU)

These are widely used in coatings and membranes for many purposes. Their chemistry is very complex, so is dealt with separately in Section 7.2.2. Molecular weights vary considerably, depending on the application. Specific gravities (SG) of film-forming PUs are between 1.05 and 1.31. Polyester PUs are used in lightweight (25–45 g m^{-2}) direct coated fabrics for rainwear. Polyether PUs are used in heavier (70–200 g m^{-2}) transfer coated fabrics that are thermoplastic in nature. Thus, they can be welded to form materials with good air or liquid-holding

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properties. Hydrophilic PUs are segmented copolymers of polyester or polyether PUs together with polyethylene oxide which form waterproof, water vapour-permeable solid films. Microporous PUs are formed by coagulation of the liquid PU in a solvent by exposure to water or steam. This forms a microporous gel structure that is then washed and dried. Both the above are used in high-performance weatherproof and protective clothing and associated personal equipment (Scott, 1995; Roff and Scott, 1971).

7.2.2   Chemistry of polyurethanes

The polyurethanes are a wide class of polymers ranging from rubbers and elastomeric fibres to surface coatings, adhesives and flexible or rigid foams. They are widely used in lightweight coated fabrics for waterproof clothing. They are derived from the reaction of polyesters or polyethers with di- or polyisocyanates to produce complex structures containing urethane linkages. The fundamental unit is based upon the urethane group:

$$
\begin{array}{c}
- \text{N} - \text{C} - \text{O} - \\
|\ || \\
\text{H}\text{O}
\end{array}
$$

Polyurethanes used in coating are complex polymers, the major component of which is a segmented prepolymer. These are composed of a linear polyester or polyether that has been extended several fold in chain length by coupling through urethane linkages. The prepolymer molecule (– PP –) can be further extended and cross-linked with a multifunctional isocyanate (– IC–) to produce the following general structure (Roff and Scott, 1971):

$$
\begin{array}{c}
- (\text{PP1}) - \text{IC} - (\text{PP2}) - \text{IC} - \\
| \\
(\text{PP3}) \\
| \\
\text{IC} \\
|
\end{array}
$$
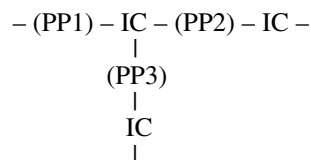
The first step in the production of complex polymers is to prepare segmented prepolymers by coupling a hydroxyl-terminated polyester or polyether to a polyfunctional isocyanate. This extends the molecular size through the urethane linkages.

  A typical polyester could be poly (diethyleneglycol adipate) with a molecular weight of between 2000 and 3000. A typical polyether is obtained by polymerisation of propylene oxide, usually in the presence of a small proportion of glycerol or sorbitol to provide branched structures. Two of the most commonly used isocyanates are 2,4- and 2,6- tolylene di-isocyanate (TDI). These are chosen because of their reactivity, cheapness and relative low toxicity. The resulting prepolymer has –OH terminal groups when a deficiency of isocyanate is used, but –NCO terminal groups if an excess of isocyanate is employed.

7.2.3   Polyvinyl chloride (PVC)

This is an addition polymer made from the vinyl chloride (CH_2–CHCl) monomer with a molecular weight of 62.5, an SG of 1.1–1.7 and a degree of polymerisation of 800–2000. PVC coating formulations must be plasticised using high boiling point esters of C_8 to C_{10} alcohols (typically phthalates, phosphates and sebacates) to render them flexible at low temperatures. PVC is resistant to acids and oxidising agents and is flame retardant, but is dissolved by many common solvents, oils and petrol. It has been widely used for heavy duty, cheap, coated fabrics, such as leather cloth, tentage, liners, truck covers, shelters, awnings, etc.

7.2.4   Polyvinylidene chloride (PVDC)

This is similar to PVC, but made from the monomer 1,1-dichloroethylene ($CH_2 = CCl_2$). It has a specific gravity of 1.67–1.71 and a degree of polymerisation of over 200. The molecular weight of commercial polymers is about 20 000. It is often used in the form of a copolymer with vinyl chloride or ethyl acrylate to improve its properties. Coating formulations are plasticised with highly chlorinated aromatics, as common plasticisers are ineffective.

7.2.5   Polyethylene (PE)

PE has one of the simplest fundamental units in organic chemistry, $-(CH_2-)_n$. It is produced in both a low-density (0.915–0.94 specific gravity) and high-density (0.94–0.97 SG) form. Both are prepared from ethylene (CH_2=CH_2). It is a relatively low-melting point polymer (130–140 °C). PE is usually prepared in film form for lamination to a range of textile structures. Products are used where resistance to solvents, alkalis, concentrated acids and oils is required. It is ideal for chemically protective clothing, especially cheap disposable clothing based upon nonwoven polyolefin substrate, a well-known example being 'Tyvek' (Du Pont).
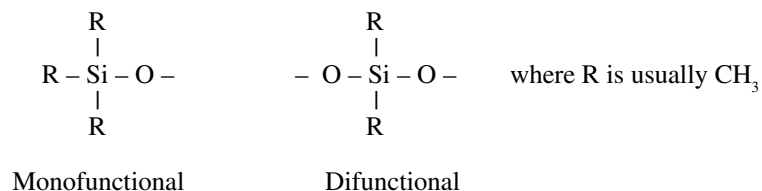
7.2.6   Polytetrafluoroethylene (PTFE)

PTFE has a remarkable range of properties. It possesses the simple monomer unit, $-(CF_2-CF_2)-$, with a molecular weight of 100, an SG of 2.1–2.3 and a degree of polymerisation of 10 000. PTFE is extremely stable and inert, is not soluble in any known liquid solvent and is unaffected by concentrated acids and alkalis. It will not burn in air, is flexible down to –80 °C and dimensionally stable up to +250 °C. It has a low coefficient of friction, good abrasion resistance and has excellent liquid repellency properties. It is predominantly available as a thin membrane that is laminated to one or more textile fabrics. PTFE is thus well suited for use against chemicals and liquids in harsh environments. One of the special uses of the membrane is in a shock-expanded microporous form, which confers high liquid barrier properties with high water vapour permeability. In this form laminates are

used in high performance wet weather clothing and equipment, under the trade name 'Gore-Tex'®.

7.2.7 Silicone elastomers

These silicon-based polymers for coatings are usually primary linear chains of difunctional polysiloxane units with monofunctional end groups as follows :

$$
\underset{\text{Monofunctional}}{R - \underset{\underset{R}{|}}{\overset{\overset{R}{|}}{Si}} - O -} \qquad
\underset{\text{Difunctional}}{- O - \underset{\underset{R}{|}}{\overset{\overset{R}{|}}{Si}} - O -} \qquad \text{where R is usually } CH_3
$$

Silicones are soluble in ketones, esters and ethers. They are unaffected by water, some mineral oils, petrol, cold acids and alkalis. They remain flexible at temperatures down to –70 °C and resist heat-ageing well. When used in thin coatings on lightweight nylon or polyester fabrics they maintain high tear strength and soft handle. When vulcanised with organic peroxides they resist microbiological attack. They are odourless, tasteless, physiologically inert and water repellent. This makes them ideal for outdoor purposes such as lightweight tents, shelters and covers. They are also used in the food, engineering and medical product industries.

7.2.8 Acrylic (polyacrylates)

Polyacrylates have the basic structure

$$
- CH_2 - \underset{\underset{COOR}{|}}{CH} -
$$
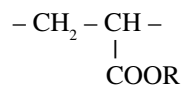
The R can be an alkyl or aryl group. The molecular weight of a typical monomer is 71, the degree of polymerisation is 5000–10000 and the SG is 1.05–1.11.

Acrylates are soluble in most chlorinated hydrocarbons, esters, ketones and aromatic hydrocarbons. They can be plasticised by esters similar to those used in PVC. Acrylate polymers used in coatings possess excellent fastness to light, weathering and microbiological attack, retaining light colours and good whiteness. The rubbers have good resistance to flex-cracking, oxidation, ozone, ultraviolet radiation and lubricating oils. These properties make them ideal for sun blinds, white hat covers and snow camouflage (Scott 2000).

7.2.9 Chlorinated and chlorosulphonated polyethylenes (Hypalon)

Chlorinated polyethylenes are prepared by passing gaseous chlorine through a hot suspension or emulsion of polyethylene in carbon tetrachloride. They contain

about 25–30% of chlorine in chlorinated groups [–CH$_2$CH(Cl)–]. Chlorosulphonated polyethylenes are similarly prepared, but both gaseous chlorine and sulphur dioxide are introduced simultaneously into the hot emulsion. They contain about 1–2% of the [–CH$_2$CH(SO$_2$Cl) –] group. The SO$_2$Cl groups provide reactive sites for cross-linking, as in the case of general purpose rubbers.

Compared with straight polyethylene, these polymers possess outstanding resistance to heat ageing and they have a degree of flame retardance. They are also highly resistant to weathering, ozone, abrasion and general chemical attack. These properties make them ideally suited for products such as tentage, chemically protective clothing, flexible fuel tanks, roofing and flooring.

7.3   Natural and synthetic rubbers

Specially compounded rubbers have been used widely for heavy duty coated fabrics. Practical rubber compounds are a complex mixture of organic and inorganic substances that must be mixed carefully to obtain uniform high-strength barrier properties. The presence of some of these compounding agents helps to identify rubber coatings. They may contain the following:

- A vulcanising agent, usually sulphur, which forms sulphur bridge bonds between the chain molecules, produces the tough practical elastomeric form.
- Accelerating agents which are usually metal oxides (MgO, PbO) or organic substances such as thiazoles, mercaptobenzthiazoles (MBT) or sulphenamides. Activators are required to make the organic accelerators function effectively. These can typically be zinc oxide and stearic acid. Stearic acid also acts as a lubricant, softener and plasticiser.
- Diluting fillers such as clays, talc, and barytes act as diluents to cut costs.
- Reinforcing fillers such as finely divided carbon black increase the tensile and tear strength of the mix. Finely divided coloured pigments can also be added instead of carbon black.
- Antioxidants such as ketone–amine condensation products or phenols are used to prevent natural ageing and atmospheric ozone cracking.

7.3.1   *cis*-Polyisoprene (natural rubber)

The simplest unit is 1,4-isoprene, although there are two distinct *cis* and *trans* isomeric configurations of 1,4-polyisoprene.

$$-CH_2 - \overset{\overset{\displaystyle CH_3}{|}}{C} = CH - CH_2 -$$
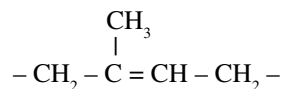
The *cis* form, where the chains substituent to the double bond lie on the same side

of the chain, is the natural elastomeric rubber used in coating formulations; the formula is C_5H_8, molecular weight is 68, degree of polymerisation is 1500–5000 and SG is 0.93.

Natural rubber is obtained by cutting (tapping) the bark of *Hevea braziliensis,* a wild tree originally found in South America. The rubber is in a milky form containing about 35% latex. The latex is separated by coagulation with a weak acid and it is soluble in a range of solvents, including hydrocarbons, chlorinated hydrocarbons, certain ketones, esters and carbon disulphide.

7.3.2   Polychloroprene rubber (neoprene)

The simplest unit is:

$$- CH_2 - C = CH - CH_2 -$$
$$| $$
$$Cl$$
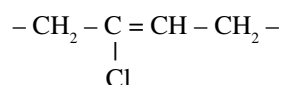
The formula is C_4H_5Cl, molecular weight is 88.5, degree of polymerisation is 1000–3500 and SG is 1.20–1.25. The vulcanised forms of polychloroprene are known as 'neoprene'. It has good resistance to heat and flames, oils, acids and ozone, which makes it useful for outdoor end-uses such as shelters, covers and industrial protective clothing.
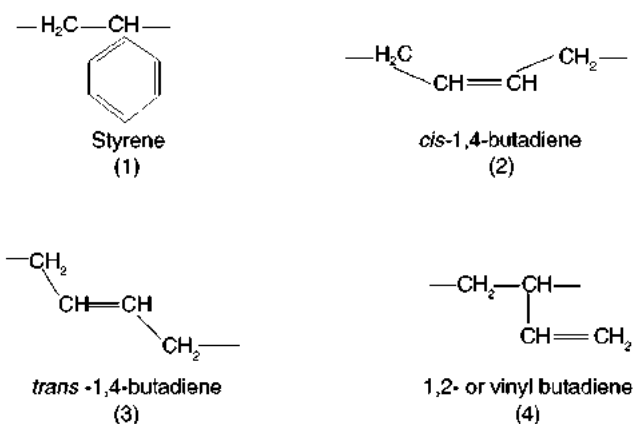
7.3.3   Polyisobutylene rubbers (butyl)

The simplest fundamental unit is based upon butylene groups attached to 1,4-isoprene units:

$$CH_3 \qquad CH_3$$
$$| \qquad |$$
$$- CH_2 - C - - - CH_2 - C = CH - CH_2 -$$
$$| $$
$$CH_3$$
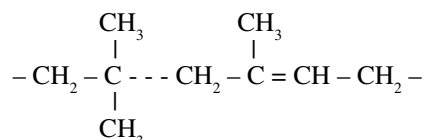
The formula for isobutylene is C_4H_8, the molecular weight is 56, the 1,4-isoprene formula is C_5H_8, molecular weight is 68, the degree of polymerisation varies from 20 to 200 and SG is 0.91–0.98.

Butyl rubber is unaffected by oxygen, alkalis, hydrogen peroxide, alcohols, phenols, animal and vegetable oils, and some ketones, ethers, esters and fatty acids. Its compact structure gives it excellent resistance to gas and liquid permeation, hence it is used in tyres, balloons, tank and pond liners. It has specialist military uses in protective clothing, covers and shelters against chemical warfare agents. The heat and flame retardance of butyl rubbers can be enhanced for protective clothing by combining small proportions of chlorine or bromine in the milling process.

Nitrile rubbers have good resistance to oils, greases and other hydrocarbon liquids and are therefore used in mechanical engineering applications.

7.4   Preparation of coatings for analysis

Ideally, it is easiest to analyse the polymer before application, to prevent any interference by the fabric substrate, adhesives or any finishing processes such as water repellency or colouration by printing. However, this is not practical on the finished coated fabric or laminate.

7.4.1   For thick coatings

When the strength of the coating exceeds the strength of the fibre/coating bond, there are several approaches:

- Using a sharp blade or grinder scrape off and discard any topical treatment, then collect subsequent scrapings or small cuttings for analysis (British Standards Institution, 2000).
- Freeze the fabric specimen down to below –20 ºC or –40 ºC then crack off the coating or membrane, ensuring that residues of fibre or finish are discarded.

7.4.2   Dissolution tests

These tests are used for thin coatings, but are also recommended for all polymer coatings and membranes to minimise contamination by substrates and finishes:

- For rubberised composites based upon natural, SBR and butyl rubbers, expose the material to the vapours of methylene chloride or 1,1,1-trichloroethane for a short time. Afterwards the solvent should be removed from the swollen rubber by drying in air at room temperature. The coating can then be carefully removed by scraping, grinding or by cryogenic crushing to pass a sieve, which has a mesh grating width of approximately 1.7 mm (International Standards Organization, 1996).
- Use a range of solvents for other polymer coatings, as detailed in Table 7.1. Tetrahydrofuran will dissolve and separate PVC and PVDC from nylon and polyester substrates in the cold. Carbon tetrachloride will dissolve and separate chlorinated polyethylene from nylon and polyester substrates. Toluene will dissolve and separate polyethylene from synthetic fibre substrates, apart from polyolefins, when the whole material should dissolve.
- An alternative method is to dissolve away the fabric substrate and leave the coating behind. Nylon can be dissolved in cold *meta*-cresol in about 1 min, or 90%v/v formic acid. Polyester (polyethylene terephthalate) will dissolve in hot *meta*-cresol, but PVC may also be affected. Alternatives are *ortho*-cresol and chloroform or *ortho*-chlorophenol.

Table 7.1 Preliminary identification tests

Appearance	Thin, clear coating	PU, acrylic, silicone, PE
	Thin white membrane	PTFE, microporous PU
	Thick, dense coating	PVC, PVDC
	Thick, dense, black/grey coating	Natural, butyl, neoprene, SBR, nitrile rubbers
Appearance under microscope	Microporous fibrillar voids or bubbles	PTFE, microporous PU
Smell	Sulphurous 'plastic' smell	Vulcanised rubbers, plasticised PVC, PVDC
Beilstein test (heated copper wire)	Blue/green flame in bunsen	PVC, PVDC, neoprene, all chlorine-containing coatings
Heating in tube	Smell of almonds (cyanide poisonous)	Acrylonitrile
	Burns with blue flame	Polyacrylonitrile
Dissolution	In tetrahydrofuran	PVC, PVDC
	In carbon tetrachloride	Chlorinated polyethylene
	In toluene	Polyethylene

• After dissolution, separate the components by filtration, washing solid residues in ethanol and/or remove the solvent by careful distillation.

7.4.3   Preliminary identification tests

A great deal of useful information can be obtained from simple tests on unknown coatings. Mere visual examination, touching and smelling the polymer can determine the type of polymer or eliminate some others. For example, PVC and many rubber coatings have distinctive colour, texture and smell. Preliminary tests are shown in Table 7.1.

7.5   Elemental analysis

These are the most important tests for additional elements other than carbon, hydrogen and oxygen. The additional elements found in coatings are nitrogen, sulphur, chlorine, fluorine, phosphorus and silicon. For many years this analysis was carried out using the sodium fusion test. However, applying this test to the mixtures that can make up coatings and laminates can cause problems. For example, nitrogen can be missed if it is present in small quantities and accompanied by chlorine, and it is said that PVC reduces the effectiveness of the fusion process (Haslam *et al.*, 1983) A more effective method is to use the oxygen flask combustion method.

7.5.1   Oxygen flask combustion method

This apparatus consists of a strong Pyrex flask fitted with a platinum gauze basket on the end of a sealed support adapter containing a platinum and tungsten wiring system through which can be passed a high-tension spark from a suitable source. In use a sample of the unknown substance is wrapped in filter paper and placed in the platinum basket. About 25 ml of 1 N sodium hydroxide solution is placed in the bottom of the flask. The flask is filled with oxygen, the electrode adapter is sealed to it, the apparatus is placed inside a suitable safety enclosure and the HF spark ignition system is activated. The sample is allowed to burn to completion, the combustion products being absorbed by the NaOH. This solution is then diluted with distilled water for further analysis.

Test for chlorine

Prepare an analar solution of 12 g ammonium ferric sulphate in water and add 40 ml of analar nitric acid. Dilute to 100 ml. Prepare a solution containing 0.4 g of mercuric thiocyanate crystals in 100 ml of absolute alcohol. Mix 5 ml of the test solution from the oxygen flask combustion method (described above) with the ammonium ferric sulphate solution. Add 1.5 ml of mercuric thiocyanate solution. When chlorine is present an orange to red colour will develop in the test sample. If a semi-quantitative estimation of chlorine is required, set the solution aside for 10 min, then measure the optical density of this coloured solution against the blank solution at 460 nm in 20 mm cells. Typical calibration figures for the examination of plastic coatings such as PVC are as follows:

Chlorine in plastic coating   = 1% up to 2%
Optical density (D20/460) measured against blank   = 0.4 up to 0.75.

Test for sulphur

Dissolve 0.2 g of peptone in 50 ml of 1% w/v barium chloride solution. Buffer to a pH of 5.0 with 0.02 N hydrochloric acid and add 10 g of analar sodium chloride, diluting to 100 ml. Heat in a water bath for 10 min at below boiling and add a few drops of chloroform, followed by filtration. This is solution A. Dissolve 0.4 g of gum ghatti in 200 ml of distilled water by warming. Then add 2.0 g of barium chloride and filter if necessary. This is solution B. Just before use, add 10 ml of A to 100 ml of B. This is the precipitating reagent C.

Transfer 5 ml of the above unknown test solution to a test tube and add 2 drops of 100 volume hydrogen peroxide followed by 1.2 ml of 1 N HCl. Mix well and add 2.0 ml of the precipitating agent C. A distinct turbidity will be produced if sulphur is present. If a semi-quantitative estimation of sulphur content is needed, add 5 ml of distilled water to both a blank and the turbid solution, mix and leave for 30 min.

Measure the optical density of the test solution in a 40 mm cell at 700 nm. Useful calibration figures are given below:

Sulphur in plastic/rubber coating   = 1% up to 2%
Optical density (D40/700) measured against blank   = 0.2 up to 0.4.

Test for nitrogen

Weigh 0.1 g of resorcinol into a clean dry beaker and dissolve in 0.5 ml of glacial acetic acid. Add 5 ml of the test solution, mix and add 0.1 g of ammonium ferrous sulphate. Prepare a blank test solution for comparison. A green colour in the test sample, compared with a pale yellow in the blank indicates the presence of nitrogen.

Test for fluorine

Prepare a buffered alizarin complexan solution by weighing 40.1 mg of 3-aminomethylalizarin-*N*,*N*-diacetic acid into a beaker and add 1 drop of 1 N NaOH followed by 20 ml of distilled water. Warm to dissolve, then cool and dilute to 200 ml. Prepare a separate solution of 4.4 g of sodium acetate in water. Add 4.2 ml of glacial acetic acid and dilute to 42 ml. Pour this sodium acetate solution into the alizarin complexan and mix to form the buffered solution.

Transfer 2.4 ml of the buffered alizarin and 20 ml of distilled water to a 50 ml beaker. Add 1 ml of test solution and mix. Finally add 2 ml of cerous nitrate solution and mix again. Prepare a similar blank solution. When fluorine is present a mauve colour will be developed in the test solution compared with a pink colour in the blank. If a semi-quantitative estimation of fluorine is required measure the optical density of the test solution against the blank at 600 nm in 10 mm cells. Useful calibration figures are given below:

Fluorine in plastic film   = 1% up to 2%
Optical density (D600/20) measured against blank   = 0.07 up to 0.135.

Test for silicon

It is important to note that any polymer coating sample used must be free from any silica fillers or water-repellent silicone surface treatment, otherwise interference will occur. However, most silicone finishes are applied to the outer textile face only.

A sample of the coating is ignited in a test tube or wet-ashed with concentrated H_2SO_4 and HNO_3. This leaves a residue of silica and the glass tube will become hydrophobic to acid and water. The presence of silicon is confirmed by:

• Adding ammonium molybdate solution to the silica residue, when a blue colour develops.
• Dissolving the residue in concentrated hydrofluoric acid. This does not leave a residue on evaporation.

Table 7.2 Classification by detection of elements

Element found	Principal coating polymers and materials indicated
Chlorine only	PVC, PVDC, chlorinated polyethylene, chloroprene rubber (neoprene), hydrochlorinated rubber, chlorinated butyl rubber
Nitrogen only	Polyurethanes, polyacrylate, polyamide, nitrile rubber (unvulcanised)
Sulphur only	All vulcanised natural and synthetic rubbers
Chlorine + nitrogen	Vinyl or vinylidene chloride/acrylonitrile copolymers
Chlorine + sulphur	Chlorosulphonated polyethylene, vulcanised chloroprene, chlorinated butyl rubber
Nitrogen + sulphur	Vulcanised nitrile rubber
Fluorine only	Polytetrafluoroethylene (PTFE)
Silicon only	Silicone elastomer or resin
Carbon + hydrogen only	Polyethylene, polypropylene, natural rubber latex, unvulcanised butyl rubber

7.6 The Burchfield colour reaction test for elastomers

The Burchfield colour reaction test is used to confirm the specific identity of a range of elastomers. The test results in colour changes before and after heating the test mixture (Braun, 1986).

In the procedure, a few grams of the finely chopped test elastomer are placed in a fusible glass tube. Another boiling tube is prepared containing 2 ml of dimethylaminobenzaldehyde solution (in hydroquinone and methanol). To this add 5 ml of concentrated HCl and 10 ml of ethylene glycol. The sample tube is then heated strongly and the vapours passed into the prepared solution. The colour change of the solution is noted after shaking and cooling. Next dilute this coloured solution with 5 ml methanol and heat for 3 min before noting the colour again. Table 7.3 gives the colour changes of several elastomers used in coating fabrics.

Table 7.3 Colour changes for elastomers in the Burchfield test

Elastomer	Burchfield colour reaction		
Polychloroprene rubber	Yellow-green	→	Dark green
Butyl rubber	Light blue	→	Violet
Natural rubber	Brown	→	Dark blue-violet
Nitrile rubber	Orange-red	→	Burgundy
Polyurethane rubber	Yellow	→	Yellow
Silicone	Colourless	→	Yellow
Styrene–butadiene rubber	Light green	→	Dark green
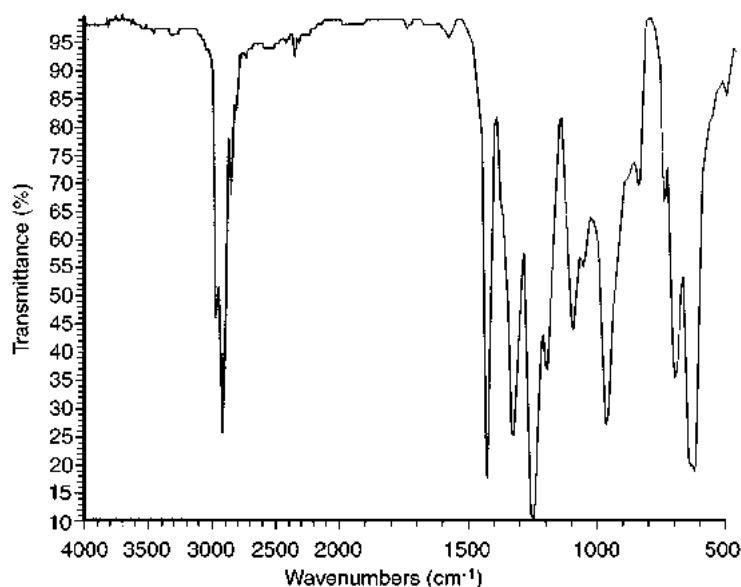
7.2 Typical Fourier transform (FTIR) spectrum of polyvinyl chloride.

7.7   Infrared spectroscopy of coatings

Spectroscopy is the study of the interaction of electromagnetic radiation with matter. Infrared radiation is absorbed by matter in the form of bands which have a discrete frequency. The nature of the absorption is related to the types of atoms present and their arrangement in the molecule. IR rays have wavelengths in the range 1–1000 μm. They are expressed as wavenumbers in cm $^{-1}$. Full descriptions and reviews of IR spectroscopy are found in (Roeges, 1994) and (Hervey, 2000). It is concluded that during the absorption process, molecules use the energy of the radiation to create or intensify vibrations in groups of atoms. The stronger the vibrating atoms are bonded together, the higher the wavenumber. The wavenumber also increases when the masses of the vibrating atoms are smaller. Each non-linear molecule displays 3N–6 fundamental vibrations, in which N represents the number of atoms of a structural unit from which the polymer, in this case, is built up. Bonds or groups of atoms can vibrate in different modes such as stretching, bending, wagging, rocking, scissoring, or as in-plane or out-of-plane vibrations, to give characteristic peaks on the graph which aid identification (Billmeyer, 1984; Geil, 1996), see Fig. 7.2 above.

A dispersive IR spectrophotometer scans the compound by means of a monochromator, and gives the absorption for each wavenumber, which is called a spectrum. A machine based upon Fourier transformation determines the absorption for each wavenumber at the same time, using a Michelson interfero-

Table 7.4 Typical infrared spectra for coating elastomers

Elastomer	Type of group vibration		Wavenumber (cm^{-1})
Polyethylene	CH_2	in-plane bend	1463
	CH_2	in-plane rocking	725
Polyacrylonitrile (PAN)	$C{\equiv}N$	stretch	2245
	CH_2	out-of-plane bend	1455
	CH	wagging	1363
Polyvinyl chloride (PVC)	Phthalate	plasticiser	1728
	CH_2	in-plane bend	1426
	CH	in-plane bend	1255
	C–C	stretch	966
	CCl	stretch	615
Polytetrafluoroethylene (PTFE)	CF_2	stretch	1220–1195
	CF_2	in-plane bend	639
	CF_2	wagging	505
Silicone	CH_3	in-plane bend	1261
	Si–O–Si	stretch	1078 & 1020
	CH_3	rocking	808
Polyurethane polyester type	NH	stretch	3400
	C=O	stretch	1730
	Phenyl	stretch	1600–1400
	NH	in-plane bend	1531
	C=O–O	stretch	1223
	O–C	stretch	1111
	N–C	stretch	1000
	CH_2	stretch	809
Polyurethane polyether type	NH	stretch	3400
	C=O	stretch	1730
	Phenyl	stretch	1600–1400
	NH	in-plane bend	1540
	CH_2	wagging	1374
	C–O–C	stretch	1110

Note: all listed except PTFE exhibit CH_3 and CH_2 stretch at 3000–2840 cm^{-1}

meter, and then generates the spectrum graphically (Kealey and Haines, 2002; Hervey, 2000).

Typical spectral peaks to aid in the identification of coating elastomers and rubbers are shown in Tables 7.4 and 7.5 (Verleye *et al*., 2001). The tables show that the infrared spectroscopic technique is invaluable in detecting characteristic peaks to identify the differences between chemically similar hydrocarbon polymers, such as polyolefins, natural and butyl rubbers. It is also sensitive enough to show the difference between polyester and polyether urethanes. Modern FTIR machines can store, retrieve and compare spectra to enable manufacturers to check quality, identity and characteristics of the polymer materials they use (RAPRA, 2004).

Table 7.5 Typical infrared spectra of vulcanised coating rubbers

Rubber	Type of group vibration		Wavenumber (cm^{-1})
Natural rubber	C = C	stretch	1645
	CH$_3$ and CH$_2$	in-plane bend	1452–1375
	CH	out-of-plane bend	886
	CH$_2$	rocking	798
SBR(Styrene–butadiene)	CH	stretch	3150–3000
	Phenyl	stretch	1600–1380
	C=C	stretch	1601
	CH	in-plane bend	1186 & 1028
	Phenyl	in-plane bend	756
	Phenyl	out-of-plane bend	697 & 540
Butyl rubber (isobutene–isoprene)	C=C	stretch	1641
	CH$_3$ & CH$_2$	in-plane bend	1470
	CH3	in-plane bend	1395 & 1365
	=CH	in-plane bend	1230
	=CH	out-of-plane bend	890
Polychloroprene	C=C	stretch	1636
	CH$_2$	in-plane bend	1458
	=CH	out-of-plane bend	884
	C–Cl	stretch	814
Nitrile (polyacrylonitrile–butadiene)	C≡N	stretch	2237
	C=C	stretch	1592
	CH$_2$	in-plane bend	1455
	C–CN	stretch	828
	CH$_2$	rocking	758

Note: All the rubbers listed exhibit CH$_3$ and/or CH$_2$ stretch peak at 3000–2840 cm^{-1}

7.8   British and international standard chemical test methods

Standard test methods that have been trialled, tested and approved by independent committees are the main methods accepted by government purchasing departments, manufacturers and quality assurance systems. Many traditional British Standards have been incorporated into International Standards (ISO) and European Norme (BS EN) standards for use throughout the world. The following list contains some of the important test methods for the chemical analysis of rubbers, plastics and other elastomers used in coated fabrics.

7.8.1   Chemical tests for raw and vulcanised rubbers

Most tests form part of British Standard 7164 (British Standards Institution, 1996; ISO, 1996).

BS 7164-2 (= ISO 4661–2) Part 2 concerns sample preparation (see Section 7.4 above)

BS 7164-6.1 Part 6 Methods for the determination of volatile matter in rubber
BS 7164-7.1 (= ISO 5945) Part 7 Methods for the determination of polyisoprene content
BS 7164-11.1 Part 11 Determination of the microstructure of butadiene
BS 7164-13 Part 13 Determination of total hydrocarbon content
BS 7164-21 (=ISO 1656) Part 21 Determination of nitrogen content (see Section 7.5.1, Test for nitrogen)
BS 7164-22.1 Part 22 Determination of chlorine content using the Parr Bomb method
BS 7164-22.2 (ISO 7725) Part 22 Determination of bromine and chlorine content using the oxygen flask method (see Section 7.5.1, Test for chlorine)
BS 7164-23.1 (ISO 6528-1) Part 23 Determination of total sulphur content (see Section 7.5.1, Test for sulphur)
BS 6057-3.25 Methods of test for synthetic rubber latices

7.8.2   Methods of test for coated fabrics and plastics

BS 3424 is entitled Methods of test for coated fabrics (British Standards Institution, 2000). There are 38 parts to this standard; most of the tests are physical tests such as strength, abrasion, flex resistance, tear, mass, thickness, ageing, liquid proofness, air permeability, and so on. However, BS 3424 Part 7 (similar to ISO 2411) covers coating adhesion strength, which includes cleaning and preparation of the coating. BS 3424 Part19 is the determination of sulphur staining. BS 3424 Part 21 is determination of fusion of PVC and state of cure of rubber coatings and BS 2782 concerns Methods of test for plastics.

7.9   Analysis of components, additives and compounding ingredients

Many coating polymers contain additives and compounding ingredients to improve the physical durability, flexibility and performance. Rubber coatings in particular usually include carbon black and inorganic fillers to improve physical properties or reduce costs.

7.9.1   Determination of carbon black in rubbers and plastic coatings.

The method involves the pyrolysis of a weighed amount of the polymer in a stream of nitrogen in an electric furnace at 300–500 ºC and is very reproducible (Haslam *et al*., 1983). The carbon residue after heating is cooled, desiccated and weighed. The percentage of carbon is determined from the original polymer sample weight.

7.9.2   Analysis of plasticisers in polymer coatings

Coatings, especially PVC, contain plasticisers to render the film coating flexible over a range of utility temperatures. There are a wide variety of plasticisers available in the form of aliphatic and aromatic phthalates, sebacates, ricinoleates, adipates, phosphates, oleates, stearates, palmitates, lactates and glycollates. Dioctyl phthalate is typically known for its use in PVC coatings.

Qualitative analysis of common plasticisers is complicated by the fact that there may be other fillers and additives in the coating polymer. It is important to dissolve out the plasticiser in a reflux apparatus with suitable solvent such as ether, methanol or carbon tetrachloride.

Phthalates can be identified by adding the acidified test solutions to resorcinol or phenol, followed by heating in an oil bath at the boil for a few minutes. After cooling and diluting, 1 N sodium hydroxide solution is added and stirred. If phthalates are present, the resorcinol test shows a pronounced green fluorescence. In the phenol test, a red colouration caused by phenolphthalein is produced. Both sebacates and ricineolates also give a faint positive fluorescence in the resorcinol test, but do not produce colour in the phenol test.

Another test for phthalates involves polarography (Whitnack and Ganz, 1953). The plasticiser is mixed with tetramethyl ammonium chloride and diluted with methanol. After removal of oxygen the solution is polarographed over the range –1.0 to –2.0 V. Dibutyl phthalate is reduced at about –1.45 V. Dimethyl, dihexyl, dioctyl and dinonyl phthalates are reduced at about –1.5 V.

Separation of mixtures of plasticisers can be achieved by thin layer chromatography on a Kieselgel plate using mixtures of benzene and ethyl acetate as solvents. The separated bands obtained can be examined by infrared techniques.

7.9.3   Analysis of fillers and pigments

Rubber compounds can contain a range of fillers such as silicates, sulphates, oxides, carbonates, phosphates, nitrates, titanium dioxide, barium sulphate and various clays. Analysis of mixtures of these additives is complicated and it is necessary to separate the constituents by dissolution in suitable inorganic solvents and/or filtration of insoluble substances such as silicates. The residues can be examined in several ways:

- Visual examination under the microscope can identify common substances such as silica (sand).
- The residues can be tested for the presence of metallic sulphates, carbonates and sulphides using inorganic analytical techniques.
- The residue can be heated until ash forms and the product is examined.
- The nature of the elements present can be established by emission and/or X-ray fluorescence spectroscopy.
- Infrared spectroscopy can be used to examine inorganic species, as many of the

Table 7.6 Infrared absorption bands for inorganic anions

Anion	Structure	Wavenumber (cm^{-1})	Comments
Carbonate	CO_3^{2-}	1450–1410 880–830	Broad and strong; split in basic carbonate
Bicarbonate	HCO_3^-	1350–1300 700–690	Broad and strong; broad medium intensity
Nitrate	NO_3^-	1410–1390 840–820	Broad and strong; sharp and weak
Phosphate	PO_4^{3-}	1100–1000	Often complex
Sulphate	SO_4^{2-}	1130–1080	Complex with strong bands
Silicate	SiO_4^{2-}	1100–900	Many silicates have complex band patterns

fillers are metallic salts in which the anion contains oxygen, i.e. in carbonates, bicarbonates, phosphates, nitrates, silicates and sulphates. Strong absorption bands due to the C–O, Si–O, P–O, N–O and S–O vibrations within the ion occur in the fingerprint regions of the IR spectrum (Haslam *et al*., 1983).

Table 7.6 shows characteristic peak wavenumbers for common inorganic anions.

7.10   Conclusions

This chapter has attempted to give guidance on the qualitative and quantitative analysis of polymeric coatings and membranes used in textiles. The coatings are often complex mixtures of polymers, composites with textile fibres, additives, finishes, fillers and plasticisers which makes them difficult to analyse without interference. Separation and isolation of a representative pure sample requires skill and a wide range of chemical techniques. Some coatings, such as PVC are relatively easy to identify by touch, smell, and rudimentary preliminary tests. Rubber coatings are relatively easy to recognise owing to their colour, smell and appearance, but analysis of the detailed composition is complicated.

Health and safety legislation is driving the coated fabric industry towards the use of less toxic, environmentally friendly processes. Many coatings are now applied from water-based pastes or as thermoplastic elastomers , so that the complications surrounding the use and recycling of organic solvents can be avoided. There is continual discussion in the western world about limiting or controlling the use of halogen-containing polymers such as PVC, PVDC and PTFE, and fillers containing heavy metals such as lead and cadmium.

Some of the identification methods must be carried out with great care and attention to health and safety considerations. Toxic vapours or gases such as HF or

HCN can be evolved as products and some additives and chemical reagents need careful handling in modern laboratory conditions. The modern textile coating and laminating industry continues to thrive and innovate, with performance requirements becoming more challenging, whilst the range of applications for high-performance technical textiles is continually increasing.

7.11   References

Billmeyer F W (1984), *Textbook of Polymer Science*, 3rd Edition, J Wiley & Sons, Chichester, UK.

Braun D (1986), *Simple Methods for Identification of Plastics*, 2nd Edition, Hanser, New York.

British Standards Institution (1996), British Standard BS 7164, *Chemical Tests for Raw and Vulcanised Rubber*, Parts 2, 6, 7, 11, 13, 21, 22, 23, British Standards Institution.

British Standards Institution (2000), British Standard BS 3424, *Testing Coated Fabrics*, Part 7 of 38 parts, British Standards Institution.

Geil P H (1996) *Modern Textile Characterisation Methods*, Raheel, M (ed.), Marcel Dekker, New York, 23.

Hall M E (2000), 'Coating of textiles', in *Handbook of Technical Textiles*. Horrocks A R and Anand S C (eds), Woodhead Publishing, Cambridge, UK, Chapter 8, 173–186.

Haslam J, Willis H A and Squirrel D C M (1983), *Identification and Analysis of Plastics*, Wiley Heyden, New York, 80–143, 326–464, 514–605.

Hervey D (2000), *Modern Analytical Chemistry*, McGraw-Hill, p 381.

International Standards Organization (1996), ISO 4661, *Chemical Tests for Raw and Vulcanised Rubbers, Part 2, Sample Preparation*, International Standards Organization.

Kealey D and Haines P J (2002), *Analytical Chemistry*, BIOS Scientific Publishers, Oxford, p 203.

RAPRA (2004), Technical Services Leaflet, Polymer Analysis Services, Rubber & Plastics Research Association, Shrewsbury, UK.

Roeges N P G (1994), *A Guide to the Complete Interpretation of Infra Red Spectra of Organic Structures*, Wiley, Chichester.

Roff W J and Scott J R (1971), *Fibres, Films, Plastics and Rubbers*, Butterworths, London, Sections 1–4, 9–12, 29–41, 56.

Scott R A (1995), 'Coated and laminated fabrics', *Chemistry of the Textile Industry*, C M Carr (ed.), Blackie Academic & Professional, Chapter 7, 210–248.

Scott R A (2000), 'Textiles in defence', in *Handbook of Technical Textiles.* Horrocks A R and Anand S C (eds), Woodhead Publishing, Cambridge, UK, Chapter 16, 425–460.

Verleye A L, Roeges P G and Moor M O (2001), *Easy Identification of Plastics and Rubbers*, RAPRA Technology, Shrewsbury, UK, 6–9.

Whitnack G C and Gantz E St C (1953), 'Polarography', *Analytical Chemistry*, **25**, 553.

8

Chemical analysis of damage to textiles

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8.1 Introduction

The chemical analysis of damage to textiles is a fascinating special area of chemical testing of textiles. It has significant practical relevance, considerable charm but also many difficulties. Determining the exact cause of damage can often be a real challenge. Those who carry out damage analysis need wide-ranging knowledge and some experience but also intuition and the ability to reason and weigh up evidence like a detective.

With a little imagination, textile damage analysis and its prerequisites can be compared to a building. The foundations consist of an extensive knowledge of textile fibres, their conversion to yarns and fabrics, dyeing and finishing, making-up processes and typical usage. Thus the base is a knowledge and understanding of textile technology, including textile physics and textile chemistry. The roof of this imaginary building is the damage analysis itself. It is supported by several rows of columns resting on the foundations. One group of columns is made up of the experience, intuition and detective-like reasoning mentioned above. The next group of supporting columns consists of the most important methods used in damage analysis, such as microscopy, chromatography, infrared (IR) spectroscopy and thermal analysis. Further supporting columns are peripheral information, starting with the conditions used in producing, dyeing and finishing the damaged textile, including the processes and machines used, further processing stages, storage, transport and, where appropriate, usage. This analogy is intended to give an idea of the requirements for successful analysis of damage to textiles and the knowledge and skills which successful analysts should have.

Analysis of damage to textiles is not usually an exact science although it does use scientific methods. In many cases several different tests are necessary. Their results can sometimes be contradictory. These then have to be evaluated and weighed up against each other very critically, whereby comparison of samples, experience with similar cases and information about the circumstances of the damage can be useful. In many ways this process is similar to a court trial when only circumstantial evidence is available but fortunately in the laboratory the damage can often be imitated and the evidence thus verified.

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8.2   Practical importance of textile damage assessment and analysis of causes of damage

Textiles can become damaged during their production as well as during distribution and usage. Experience shows that consumers are less likely to make complaints than are those people involved in the chain of textile production. For example, textile manufacturers often dispute with textile dyers and finishers about who might be responsible for faults, although this can usually be clarified quickly by means of a film imprint, as shown in Section 8.4.6. As well as the question of who is responsible and therefore who has to bear the costs, it is naturally also of interest to know how the damage can be repaired and also how it can be avoided in future. In the case of large lots or continuous production it is often important to find out very quickly what the cause is in order to stop producing the fault as soon as possible. In this respect damage analysis plays an essential role in quality assurance. Lack of quality and subsequent complaints should not be underestimated in terms of the image problem they present for the supplier. Experts in damage analysis are thus often employed by well-known companies.

In spite of modern process control, optimization and quality control faults cannot be avoided completely. They occur at all stages of textile production including storage and transportation. The experts in damage analysis at the fibre, dyestuff and auxiliary agent producers, as well as those at the testing and research institutes, still have their hands full, dealing with many cases of damage where the costs caused by the fault can be quite high. Some disputes about damage are settled by a court but more usually the customer and producer agree on a settlement. Depending on the importance of the business relationship, fair dealing and price discounts play an important role here. Occasionally unjustified complaints are also made in the hope of obtaining just these benefits. In order to remain in charge of investigations of complaints, most of the West European producers of fibres, dyestuffs and auxiliary agents have their own testing laboratories with damage analysis experts. The alternative, namely to let testing institutes carry out this work, is usually rejected because, amongst other reasons, the companies would have to reveal too much detailed knowledge and also because it often takes too long. Some producers of textile auxiliary agents choose another, risky path. They take care of complaints simply by giving price reductions without carrying out their own laboratory investigations.

Most textile companies do not have the personnel or equipment required for the clarification of complicated faults. On the other hand they do have the best insight into peripheral information required for damage analysis. However, when they hand over the fault to an institute or, more usually, to their suppliers of fibres, dyestuffs or auxiliaries for investigation they often only pass on part of this information. Analysis of the fault is then often regarded as technical customer service in order to promote and cement customer relationships. The intensity of

these external analyses of damage then sometimes reflects that of the business relationship.

Although there are no figures available for the economic importance of textile damage analysis it can be roughly estimated from the expenses incurred by producers of fibres, dyestuffs and auxiliary agents in dealing with complaints and analysing damage. These expenses for personnel and equipment are very high even though some decades ago they were even higher. The authors know of at least two dozen specialized laboratories that undertake such analyses in German-speaking countries, in industry and in testing and research institutes. If it is assumed that on average two or three employees are involved with a corresponding annual budget of about 300 000 to 400 000 euros per laboratory this would amount to a total of up to 10 million euros just for Germany, Switzerland and Austria.

8.3   Fundamentals of textile damage analysis

8.3.1   Definition of faults, damage and quality

Faults are defects which lower the value and usefulness of goods. According to DIN 40 080, faults are defined as any kind of deviation from prescribed require-ments. Damage is the disadvantage arising from faults. Thus damage analysis is a wider ranging term than analysis of faults. It is damage which leads to complaints and, as a rule, to demands to repair the damage or compensate for it. Quality is defined as the total sum of characteristics relating to suitability in use, which fulfil defined and prescribed specifications. Damage analysis is an important part of quality control and contributes to quality assurance.

8.3.2   Manifestations of damage

The manifestation of damage to textiles can vary widely. It ranges from obvious, for example visible or easily recognizable defects, to hidden ones, for example defects that are hard to detect or those that can only be detected later. It is the latter type which is generally the reason for giving guarantees.

Perception and description of the fault are the first steps in damage analysis. Damage can be perceived visually, macro- and/or microscopically, often only with a specific type of illumination, such as reflected, oblique or transmitted light, or with a specific light source, for example ultraviolet (UV) or polarized light. Some faults are detected by other senses, usually in the form of a handle assessment, or they can be registered by measurements. Examples for the latter are colour measurement, tensile and abrasion strength, extensibility, shrinkage and fastness properties. These technical properties can be supplemented by thermophysiological comfort properties and care requirements, where significant deviations from the agreed or specified values can be claimed as faults.

Damage is manifested most commonly as stains followed by streaks and

barriness. Other types of damage manifestation, such as differences in hue or depth of shade, unlevelness of dyeing, lack of strength, deposits, abrasion and holes, occur with less frequency.[1]

It is important here to describe the fault as exactly as possible. All the typical characteristics and peculiarities, their frequency and possible regularity have to be noted and also whether they can be localized to individual fibre or thread systems. This makes it easier or even possible to determine the cause of the damage later.

8.3.3   Damage causes

There are mechanical, thermal, chemical and biological causes of damage to textiles. They may be attributed to different causal agents, in particular to textile manufacturers, dyers and finishers, garment producers, distributors or consumers. Although there are cross-relations between all the above-named causes and other causal agents, it is usual, for example, to attribute mechanical damage to the textile manufacturer and chemical damage to the dyer and finisher.

Although there are different types of damage manifestation, there is no especially typical cause of damage. In the statistical investigation, based on 550 cases of damage, there were 81 different causes of damage where more than 10 cases were registered. Their proportion ranged from 2% to a maximum of 6%.[1] Other sources also report a similarly wide range of damage causes with a relatively low percentage in each case.[2] This enormous range of causes is typical for damage to textiles and makes its analysis difficult.

This statement is also applicable to the causes of the most frequent manifestation of damage, namely stains. Statistical analysis of 258 cases of damage by stains resulted in 29 types of cause, each represented in more than seven cases.[1] The most common types of cause gave frequencies in the range from 7–8%. These are, for example, stains caused by mechanical and chemical influences, dyestuffs, grease or oil, silicone and dead or immature cotton.

8.3.4   Chemical and physical assessment of textile damage

Of the many possibilities for investigating damaged textiles, two main groups can be ascertained: chemical and physical testing. Corresponding to this, two types of textile laboratories are often to be found, namely chemical and physical testing laboratories. Each offers different advantages for damage investigation. Physical testing does not require any chemicals and often gives results which are easily interpretable and may allow a direct quality assessment such as 'just acceptable', 'second choice' or 'reject'. On the other hand with chemical testing the cause of the damage can be ascertained, which is what is actually meant by analysis of damage. But this advantage often has to be paid for in the form of higher costs for personnel and equipment.

8.3.5   Procedure for textile damage analysis

Unfortunately there are no hard and fast rules on how to proceed with textile damage analysis. The variety of cases and causes is too great for this. Nevertheless, some companies and institutes use their own preprinted forms with long lists of tests for this purpose. This has the advantage that none of the rare tests is overlooked but also the disadvantage of inflexibility and unnecessary work on certain types of damage. Such preprinted forms may be of help to less experienced testers but experienced testers tend to have their own specific procedures, depending on the case, and are often guided by their intuition. As a general rule preliminary tests are made, followed by more painstaking specific tests.

   The usual steps taken in an investigation are illustrated here using the example of stain analysis:

1. Manifestation of the damage with a description of the type, distribution and possible regularity of the stains
2. Microscopy with increasing magnification, beginning with a magnifying glass or stereomicroscope and progressing to 300 to 1000-fold magnification. Use of different types of illumination and contrast, such as reflected, oblique and transmitted light, UV, polarization or fluorescence
3. Preliminary tests such as solubility and staining tests
4. Isolation of the substance causing the stains (for example by extraction in a Soxhlet apparatus) and concentration of the extraction residue. It is recommended here to cut out the stained areas from the specimen and to extract an equivalent quantity of unstained material for comparison. If the stain is in the form of insoluble deposits an attempt can be made to dissolve the fibre material and thus isolate the stain substance
5. Comparison and identification, usually by means of thin layer chromatography and/or IR spectroscopy. Comparison is made with the blank sample (extract from unstained areas) and with authentic substances which could have caused the stain. If the stain cannot be extracted, IR spectra from stained and unstained areas can be compared and the spectra subtracted in order to identify the stain substance. The limits of detection of typical stain substances in IR spectra and a comparison of IR methods have been given in the literature[3,4]
6. Reproduction, if possible, of the damage in order to verify the findings, for example comparison with authentic stain substances on the same textile material, using conditions as close as possible to those used with the damaged sample
7. Further verification, for example, if possible, by means of consultation with the persons concerned in the stage of production suspected of causing the damage. It is important here to consider alternatives and to test the plausibility of the findings critically
8. Summary of the findings, discussion of the results. If the cause has not been clearly identified the results should be formulated carefully and alternatives mentioned. Documentation including photographs and possibly samples.

9. If possible hints should be given on how to avoid such stain formation in future and also on how to remove the stains (suitable solvents and procedures).

The last steps in this stain analysis demonstrate that comparative samples and information from peripheral areas of the case can be particularly useful aids in damage analysis. An archive with similar cases of damage can also be very useful here. If the archive is very extensive, retrieval of information on all damage cases according to different criteria should be possible, such as type of textile and fibre, damage manifestation, cause of damage, method and procedure leading to clarification and, if available, the source and client for the analysis.

In many cases, but unfortunately not in all, about halfway through these steps, or at least after the preliminary tests, the cause of the damage may be suspected and this may lead to a working hypothesis. This hypothesis then has to be either unequivocally verified or rejected on the basis of further tests. It is often hard to give up a hypothesis and look for a better one. Self-criticism and experience can be helpful here as well as literature searches and discussions with interested colleagues or other experts.

8.3.6   Literature on textile damage and its analysis

A very useful book, in which many typical cases of damage are described and illustrated, has been published by Mahall.[5] In this book he has summarized his years of experience in damage analysis and his many publications in such a way that readers receive valuable stimulation for their own work. Further books which may be of assistance in damage analysis include those from Hearle *et al.*,[6] Agster,[7] Stratmann,[8] Greaves and Saville[9] and from the Textile Institute.[10]

Most of the articles on damage analysis published in journals are not recent.[11–21] This is also true of company brochures on this topic.[22–24] In the selection mentioned here, the last article is cited if it is part of a series of articles. Citations for previous articles in the series can be obtained there.

8.4   Methods of textile damage analysis

8.4.1   Preliminary examination

The subject of preliminary examination is as varied as a later part of this section, namely miscellaneous methods. There may also be no clear-cut separation between the two. Preliminary examination is composed of simple tests, carried out in a short time and with little effort, which give the first clues in damage analysis.

It is usual to begin with an exact visual examination, if possible in comparison with an undamaged sample. Notice should be made of any peculiarities in appearance. Sometimes abraded and raised areas, holes, thin places and pressure marks can be easily recognized without optical aids. With the use of a magnifying glass they can be seen more clearly and in more detail. The same is true for many

visible deposits of foreign matter such as silicates, calcium and magnesium salts (for example oxalate, phosphate), polyester oligomers and mildew spots.

As a next step, easily determinable differences between the damaged sample and undamaged comparison samples can be sought, for example handle assessments, wetting behaviour (TEGEWA drop test[25]) or pH value. The latter can be determined with moist pH paper or more accurately by adding a drop of liquid indicator or with a flat-bottomed pH electrode. The microscopical detection of acid residues by the formation of methyl orange crystals is described in Section 8.5.2. Simple tests of mechanical strength (stretching between the thumbs), crocking fastness tests (dry and wet) and, where appropriate, a test of wet fastness, for example in cold and then heated dimethylformamide, also belong in this group.

After marking the damaged area, woven fabrics can be separated into warp and weft threads and knitted fabrics unravelled in order to investigate the isolated threads more thoroughly. Do the threads from the damaged area show differences in diameter, twist level or yarn composition? Are stray fibres discernible?

Rapid methods of separating fibre blends for damage analysis

Part of the preliminary examination of textile blends consists of dissolving out one fibre component and examining the residual fibre to see which fibre components are damaged. The following methods of separation have proved useful:

1. Polyester residue in blends with cellulose, acetate or nylon: The sample is treated with 72% sulphuric acid for 5 min at 70 °C or in 75% sulphuric acid for 20 min at 50 °C. It is then thoroughly rinsed with water, neutralized with diluted ammonia, rinsed again and dried. (Acrylic fibres may dissolve.)
2. Polyester residue with polyester/wool blends: The sample is boiled for 1–2 min in 3.25% caustic soda, then rinsed with water, neutralized with diluted acetic acid, rinsed again and dried.
3. Cellulose or wool residues in blends with polyester fibres: Dissolution of the polyester fibre is carried out in a 50% solution of trichloroacetic acid in chloroform at room temperature for 15 min (liquor ratio 1:50). The sample is then rinsed twice with about 100 ml of a 15% solution of trichloroacetic acid in chloroform. The sample is subsequently rinsed with cold chloroform until, in the case of dyed samples, the solvent is no longer dyed. As a rule about 200 ml of chloroform are required. A final rinse is made with hot water.
4. Nylon residue with nylon/wool blends: The wool is dissolved with caustic soda as in method 2.
5. Wool or cellulose residues in blends with nylon: The nylon fibres are dissolved out by treating the sample two to three times with concentrated formic acid for 15 min each time at room temperature. The sample is then thoroughly rinsed with concentrated formic acid, hot water, diluted ammonia and cold water and then dried.

6. Acrylic residue with acrylic/wool blends: The wool is dissolved with caustic soda as in method 2.
7. Cellulose, wool, nylon or polyester residues in blends with acrylic fibres: The fibre sample is treated at 90–100 °C for 1 h in dimethylformamide, preferably in a boiling water bath. The fibre residue is then extracted with fresh dimethylformamide for 30 min in the boiling water bath. It is then washed with 1–2 l of hot distilled water and dried.
8. Diacetate fibres can be dissolved out by two treatments with acetone and triacetate fibres by three treatments with dichloromethane, in each case for 10 min at room temperature. In this way they can be separated from cellulose, wool, silk, polyester or acrylic fibres, which then remain as a residue.
9. Wool and silk fibres can also be dissolved out by treating with sodium hypochlorite solution for 20 min at room temperature (35 g l^{-1} active chlorine and 5 g l^{-1} caustic soda), followed by rinsing, anti-chlorine treatment with natrium thiosulphate solution and further rinsing. Cellulose, nylon, polyester, acrylic or polyvinylchloride fibres remain as residue.

Fibre identification

Determination of the fibre type, including checking of the stated fibre type, is one of the most important preliminary tests. If no IR spectrometer is available, standard fibres can be most readily identified using the characteristic reactions according to Stratmann.[8] For modified fibres or high-performance and speciality fibres the more complicated classification on the basis of solubility groups and their sub-divisions[8, 26] or other methods of analysis[27] have to be used.

Qualitative analysis of standard fibres by means of microscopy and characteristic reactions can be carried out as follows:

1. Wool can be easily recognized in the longitudinal microscopic view on account of its typical scales.
2. Cotton has typical irregular convolutions in the longitudinal microscopic view. When raw cotton is embedded in cuoxam the fibres show a typical balloon formation.
3. Flax is stained blue by zinc chloride–iodine reagent (see Section 8.5.6), as are all other cellulose fibres. In addition the typical V- and X-shaped transverse structures can be seen more clearly. Differentiation from hemp can be made by means of a cross-sectional sample. Flax shows clearly visible irregular polygons with lumen, hemp shows relatively indistinct and often conglomerate structures.
4. Viscose shows typical longitudinal striations in the longitudinal microscopic view. Cupro, lyocell and some polynosic fibres have round cross-sections and can be confused with mercerized cotton, which, however, appears more irregular. Lenzing modal fibres can be recognized by one clearly visible longitudinal striation. Further helpful details are described by Reiter.[28]

5. In the longitudinal microscopic view raw or degummed silk appear as double or single filaments, respectively. Silk gum residues can be visualized by staining with direct dyes or Neocarmin W (see Section 8.5.3). Silk dissolves in cuoxam as do the cellulose fibres. It can be distinguished from them by the lack of blue staining in the zinc chloride–iodine reagent and by its irregular longitudinal form.

6. Cellulose di- and triacetate fibres (CA, CT) as well as acrylic fibres (polyacrylonitrile, PAN) are all soluble in the zinc chloride–iodine reagent. An initial differentiation is made using the acetone test on a watchglass: only CA and CT fibres dissolve (evidenced by a cloudy evaporation residue). Differentiation between CA and CT fibres: CA dissolves in Frotté II reagent (see Table 8.1), CT only swells. Results are similar in zinc chloride/formic acid, but with a less distinct difference (CT swells more markedly). PAN fibres dissolve in cold concentrated nitric acid and in dimethylformamide at 100 °C. They swell in boiling 85 % formic acid and decompose at about 280 °C without melting.

7. The nylon fibres PA 6 and PA 6.6 show the typical crenellation of the fibre surface in Frotté I reagent after maximally 5 min at room temperature. In the weaker Frotté II reagent this reaction only occurs with PA 6 (see Table 8.1). Further differentiation is by determination of melting point (PA 6 = 215 °C, PA 6.6 = 255 °C, PET also at 255 °C).

8. When polyester fibres (polyethylene terephthalate, PET) are heated in 15% alcoholic potassium hydroxide (KOH) on a microscope slide with a cover slip, typical needles are formed from the potassium salt of terephthalic acid.[29] This characteristic reaction for polyester is simpler and less problematical than the staining of fibre ends with Oil Red in *m*-cresol as described by Stratmann.[8]

9. Polypropylene (PP) and polyethylene (PE) fibres float in water, they are not soluble in cold concentrated sulphuric acid but soluble in boiling perchloroethylene. They are also easily recognizable and distinguishable by their melting points: PE 124–138 °C (occasionally up to 155 °C) (low density PE 105–129 °C), PP = 160–175 °C (if based on metallocene catalysis 15–20° C lower).

10. Elastic fibres can be easily recognized by their great extensibility and elasticity as well as their longitudinal microscopic view (often quasi-monofil from coalesced single fibrils). As opposed to rare rubber threads, elastane fibres based on polyurethane dissolve in boiling dimethylformamide and swell markedly in 85% formic acid.

Further preliminary tests

Sometimes it can be appropriate to carry out preliminary tests for readily detectable elements or compounds, for example the Beilstein test for organically bound

Table 8.1 Frotté reagents and reactions (according to Stratmann[8] except acetylated polyvinyl alcohol fibres)

Reagent	Main reaction	Side reactions
Frotté reagent I 100 g anhydrous $ZnCl_2$ are dissolved in 50 ml water and the density adjusted to 1.900 (g cm^{-3}), then 5 parts by volume of this solution mixed with 1 part by volume of methanol	Frotté reaction (crenellation) within 5 min at room temperature with nylon 6 and nylon 6,6; with nylon 11 and nylon 12 the reaction only occurs after heating on the microscope slide until boiling	Swelling with regenerated cellulose fibres, dissolution of acetate and acrylic fibres, swelling reaction with polyvinyl acetate fibres, swelling and core contraction reaction with acetylated polyvinyl alcohol fibres resulting in a characteristic zigzag form
Frotté reagent II 100 g anhydrous $ZnCl_2$ are dissolved in 100 ml water and the density adjusted to 1.566 (g cm^{-3}), then 5 parts by volume of this solution mixed with 1 part by volume of methanol	Frotté reaction (crenellation) within 5 min at room temperature with nylon 6 (not with nylon 6,6, nylon 11 or nylon 12)	Swelling with regenerated cellulose fibres, differentiation of acetate fibres: CA soluble, CT only shows swelling, swelling reaction with polyvinyl acetate fibres, swelling and core contraction reaction with acetylated polyvinyl alcohol fibres resulting in a characteristic zigzag form

chlorine (green coloration of the flame when heating a copper wire with a small fibre sample in the non-luminous region of a gas flame). In this way fibres containing vinyl chloride can be easily recognized.

A further example is the detection of iron in the combustion residue of a textile sample or directly on the fibre material. For example, after adding a few drops of 1 N hydrochloric acid p.a. and 1 N ammonium thiocyanate a red iron complex is formed which can be concentrated by extraction with ether so that the detection limits are very low (more detailed description in Section 8.5.1).

Hints on the presence of silicone deposits are given by the adhesive strip test (lowering of the adhesion due to silicone) and the foam test (marked formation of foam when the textile sample is shaken with chlorinated hydrocarbons). Detection by means of IR spectroscopy is discussed in Section 8.4.4.

Staining, swelling and solubilty tests as well as extraction are seldom so simple that they might be included under preliminary examination. As a rule they belong to the miscellaneous methods discussed in Section 8.4.6.

8.4.2   Microscopy

Microscopy is certainly the most important method used for damage analysis of textiles. Without microscopy and its supporting techniques the elucidation of most cases of damage would not be possible. The extensive literature on this topic also demonstrates the great importance of textile microscopy for damage analysis.[5, 6, 8–13, 22, 24, 30–38] A number of well-known textile microscopists who also worked intensely on elucidation of faults deserve mention here: A. Herzog (Vienna, Dresden), H. Reumuth (Jena, Mannheim, Karlsruhe), P.-A. Koch (Dresden, Zurich, Krefeld), M. Stratmann (Krefeld), N. Bigler (Basle), K. Mahall and I. Goebel (Düsseldorf) and G. Schmidt (Ludwigshafen).

Microscopical methods are used in the textile industry to investigate raw materials, for product development and analysis of competitor's samples, and to check production and control effects and quality. Typical examples of their use are shown in Table 8.2. Textile microscopy is indispensable in dealing with complaints and analysing damage as well as in avoiding faults and repudiating unjustified claims. Microscopy is, of course, just as important in textile research (for example in the analysis of the fine structure of fibres, surface modifications and investigations on the distribution of dyes and auxiliaries).

Stereo microscope

The microscopical investigation of damage usually begins with a stereo microscope at low magnification (about 5X), which can then be increased to about 100X. If necessary the damaged areas can often be marked and thus distinguished from their intact surroundings. The large distance between sample and objective enables individual threads, foreign fibres or deposits to be easily manipulated. Further advantages of the stereo microscope are the spatial, three-dimensional image obtained and the fact that different types of illumination can be readily used, depending on what is to be examined. For example, reflected light falling obliquely from one side or opposite sides can be used as well as even, shadow-free illumination with a ring lamp or contrasts with strong shadows using extremely flat illumination from one side. Transmitted light is also possible with the stereo microscope but is seldom used in damage analysis.

Compound microscope

More detailed information can be obtained from light microscopes with up to 1000X total magnification. They are also known as compound microscopes because they have two complementary light paths, the illuminating and the imaging light path, which are adjusted to each other by means of the condenser and aperture diaphragms (Köhler illumination). Such microscopes are available with transmitted light for single fibre investigations or for thin cross-sections and with reflected light for non-transparent objects. Brightfield illumination is usually used

Table 8.2 Examples of the use of microscopy in textile production and fault analysis[35]

Production stage	Examples
Primary spinning	Cross-sectional form
	Fineness
	Delustrant
	Vacuoles
	Drawing
	Core-sheath structure
	Bicomponent fibre structure
Secondary spinning	Fibre identification
	Blend distribution
	Hairiness
	Twist
	Slubs, neps
	Fibre slippage
	Variation in thickness
Texturizing	Type of texturizing
	Fibre deformation
	Bulking effect and evenness of bulk
Weaving preparation	Distribution of size
Weaving and knitting	Fibre type and state
	Weave/knit pattern and pattern faults
	Deposits, waxes, grease
Pretreatments	Fibre type and state
	Degree of alkalization, mercerization, saponification
	Bleaching effect, bleaching damage
	Mechanical effects such as extent of raising, pile position
Dyeing	Evenness, macro- and micro-levelness
	Penetration
	Deposits
	Migration
	Bicolour effect with blends
Printing	Clarity of print
	Print penetration
	Distribution of binder
Finishing	Distribution
	Crosslinking
	Mechanical effects such as chintz, embossing, raising, emerizing

with transmitted light. Darkfield illumination allows edge structures such as projecting fibres from yarns, scales on animal hairs and delustrants to be more easily observed. Polarized light is used for the determination of the melting point of synthetic fibres (see Section 8.4.5), for their identification by means of birefringence and also for damage analysis.[39] Differences in tension and drawing as well as fibres deformed under pressure can be seen more easily between crossed polars. The same is true for the typical transverse structures in natural fibres, such

Table 8.3 High-magnification microscopic methods for textiles: types of contrast and illumination[40]

Method, contrast	Reflected light	Transmitted light
Brightfield	Seldom	Very common
Darkfield	Seldom	Common
Polarization	Very seldom	Common
Fluorescence	Common	Seldom
Scanning electron microscopy	Common	Seldom

as ramie or tussah silk.[38] Phase contrast and interference contrast methods are very seldom used in microscopical investigations of textile damage. For fibre identification with polarization and interference microscopy, see Section 8.7.1. The usual contrast and illumination methods at high magnification as used here are summarized in Table 8.3.

Fluorescence microscopy

In damage analysis the most important microscopical contrast method is selective staining of structures of interest. Unfortunately there are cases where no normal dyes are known that give selective staining. However, if selective staining with fluorescent dyes is successful, fluorescence microscopy can be a particularly useful method of investigation for the analysis of damage to textiles. It is more or less independent of the original dyeing of the textile and it can create strong contrasts and thus mark substances present in low concentrations. In rare cases the natural fluorescence of the material can be sufficient for the investigation, for example with wool where it occurs in direct relation to yellowing.[41] However, the samples are usually selectively stained with fluorescent dyes, the so-called fluorochromes. The exciter and barrier filters of the microscope then have to be adjusted for the particular fluorochrome. Otherwise the relatively weak fluorescence would be superimposed by the intensive excitation light. The best-known excitation is with UV light for optical brighteners, which then emit blue light. In this case a barrier filter which does not transmit UV light is necessary. Further examples are shown in Table 8.4. The most common method of illumination in fluorescence microscopy is the reflected light/brightfield method. In sample preparation care should be taken to use non-fluorescent embedding agents and extremely clean slide glasses and cover slips so that the background is not brightened by dust, scratch marks, fingerprints or similar. Although this suggests that expensive apparatus and time-consuming sample preparation are required, the following examples will serve to show that the effort is worthwhile. These examples are directly or indirectly related to damage analysis.

Hesse and Pfeifer[43] described the fluorescent detection of oil stains, the analysis of the distribution of optical brighteners in polyester/cotton blends and the

Table 8.4 Examples of the relationship between excitation range, object colour and fluorochrome[42]

Excitation range (nm)	Excitation colour	Fluorescence/object colour	Examples of fluorochromes
340–380	UV	Blue	Optical brighteners
450–490	Blue	Yellow to yellow-green	Auramine (C.I. Basic Yellow 2)
515–560	Green	Red	Rhodamine B (C.I. Basic Violet 10) Phloxine B (C.I. Acid Red 92)

detection of photolytic damage by means of macroscopical and microscopical fluorescence techniques. Nettelnstroth showed how several cases of damage arising from fibres with different degrees of optical brightening could be elucidated with the aid of fluorescence microscopy.[44] Meyer and Zürcher were able to analyse the distribution of cross-linking agents in cotton by means of bicolour fluorescence, whereby the cross-linked areas were stained with Rhodamine B and the non-cross-linked areas with an optical brightener.[45] Meyer was able to visualize the distribution of anti-felting agents on wool by means of bicolour fluorescence, including the use of a filter dye which lessened the disturbance caused by stray light.[46] Based on this work further publications have dealt with the investigation of dye transport in wool[47] and polymer distribution (for example silicones) on wool.[48, 49] On account of the natural fluorescence of many kinds of fungi, biological damage to textiles could be analysed.[50, 51] The distribution of applied spin finishes has been studied with fluorescent staining.[52] Amongst the many publications in which the diffusion of dyes, surfactants and other substances in textile fibres has been studied using fluorescence microscopy, those of Lewis and Smith, in which the role of reactive dyes in the prevention of damage to wool are described, may be mentioned here.[53, 54] Use of fluorescent marking to check the distribution of binding agents applied to nonwovens[55] and the fibre-dependent distribution of silicones[42] has been described.

Scanning electron microscopy

Because of the high costs of equipment and personnel, including sample preparation (sputtering or vaporizing with carbon or gold in high vacuum), scanning electron microscopes (SEM) are seldom used for damage analysis of textiles. Only black and white images can be obtained and the staining, swelling and dissolution reactions which play such an important role in light microscopy are not possible with SEM. On the other hand SEM offers considerable advantages. Because of the very short wavelength of the electrons used, much greater magnification is possible than with light microscopy. More importantly for damage analysis, SEM images have a large focal depth and appear strongly contrasted and spatial. For example, with SEM determination of the cuticle height, wool (0.6 μm) and mohair

or cashmere (0.4 μm) fibres can be differentiated and quantitatively analysed in wool/mohair or cashmere blends.[56] SEM combined with energy dispersive analysis (EDA) can detect elements quantitatively with atomic numbers of 11 (sodium) or higher on the sample surface. Thus, for example, delustrants, heavy metal, phosphorus or chlorine content, and deposits of silicone, silicates or calcium salts can be analysed.[57, 58]

Microphotography and image analysis

To conclude this section on microscopy textile in damage analysis the production of cut or ground cross-sections should be mentioned. Also, surface imprints of fibres, yarns and fabrics, which are of such importance for damage analysis, are usually, but not always, evaluated microscopically. They are therefore discussed in Section 8.4.6. Illing-Günther and Hanus[37] analysed spots using microspectrophotometry. Finally, digital image analysis, which has now reached a high stage of development, should be mentioned, since it allows easy evaluation, archiving and distribution of microphotographs. The demands made on good micro-images are almost self-explanatory. They should show the object of interest as sharply as possible and with high contrast; as a rule they should not be manipulated, although selective colouring can be used to highlight the object, and the microphotographs should be evenly illuminated.

Cross-sections and grinding techniques

Cut or ground cross-sections of fibres, yarns and fabrics are of interest for fibre identification, in fault analysis in primary and secondary spinning and in checking the penetration of dyes into fibres, filaments, yarns and fabrics. These methods are also used to investigate hollow and multicomponent fibres, the build-up, adhesion and evenness of coating layers and the analysis of other textile composites. All of this can be useful for damage analysis. Grieve[59] has written a review on cross-section preparation methods for fibres.

   If high-quality images are not required simple, rapid methods are advantageous, for example manual cross-sections using the cork or metal plate methods[28, 32] or the ITF or Hardy hand microtome.[60] The wet grinding methods developed by Rohner and Wagner[24, 61–63] have proved useful, where normal buttons are used for smaller samples and easily prepared small Perspex plates are used for larger samples. The samples are fixed with rapid adhesive in the holes of the button or the ridges of a Perspex sandwich. By grinding with increasingly fine-grained emery paper, high-quality thin sections can be obtained in 10 to 20 min. These provide long-lasting microscopic slides. Even fibre types which cannot be cut smoothly or easily, such as aramides and other high-tenacity fibres, glass and metal fibres, can be easily prepared as microscopic cross-sections in this way. However, with fibres which swell greatly in water there is a danger that after prolonged wet grinding the thin sections break away from the glass slide.

Cross-sections of particularly high quality are made with rotary or slide microtomes. A rotary microtome controlled by foot has the distinct advantage that both hands are free to take up the delicate thin sections with tweezers and paintbrush. Before they can be cut, textile samples have to be embedded. The embedding agent should as far as possible be transparent and colourless. It should not damage the sample or alter it, for example by heat of polymerization, or by dissolving, swelling or staining it and its hardness should be as close as possible to that of the fibre to be cut. If the embedding agent is too soft, the fibre is dislodged laterally when cutting, if it is too hard the thin sections become brittle and break and the microtome blades have to be resharpened too often. It is also important that there is good adhesion between the embedding agent and the fibres. In addition, air bubbles must be avoided or else they must be easily removable before hardening takes place (wetting behaviour and viscosity). In the authors' laboratories three polymer systems have proved their worth for this purpose.

1. Mixtures of the methyl and butyl esters of polyacrylic acid

The methyl ester of polyacrylic acid is relatively hard whereas the butyl ester is soft. By varying the proportions of these two esters the hardness of the embedding copolymer can be made to suit the fibre to be cut. For example, Peter[24] recommended a mixture of methyl and butyl ester in the ratio 30:70 for cellulose and nylon fibres and 40:60 for the harder polyester fibres, and 1% of dibenzoyl peroxide is added as a catalyser. Polymerization then takes place for 4 h at 70 °C in a water bath. The water bath initially supplies the heat required for the start of polymerization but it then has the advantage that it quickly takes up the heat of polymerization and prevents overheating of the sample. Peter used aluminium tubes as the form for the reaction since these could be easily bent to hold cardboard frames. The fibres, yarns or fabrics are stapled under tension to the frames. Disadvantages of this embedding system are the marked odour of the monomers and the fact that they have to be separated from their stabilizers before use. During mixing they have to be stirred carefully to avoid air bubbles. Such bubbles can be removed by short evacuation in a low vacuum; under high vacuum the monomers evaporate.

2. Epoxide resin (for example Araldite D with 20% hardener HY 956 from Ciba)

At room temperature the polymerization of this embedding system lasts about 10 h; at 70 °C in a water bath it only lasts 1 h, with the additional advantage of protection against overheating as mentioned above. The handling is easier (no removal of stabilizers) but the hardness cannot be varied. Peter recommended use of this embedding agent when the acrylic acid esters dissolve the fibres or dyes.[24] However, disperse dyes are also taken up by epoxide resins so that the dyed fibres become lighter.

3. Embedding agent hardened by light (Technovit 200 LC[64])

This embedding agent based on mono- and difunctional methacrylate does not

need to be mixed and hardens in 30 min after illumination with blue light. In daylight and the usual forms of artificial light the medium is relatively stable so that there is enough time for preparation. It is odourless and does not form bubbles or cracks. A special advantage is the possibility of building up the embedded sample in layers, making it easier to hold the sample or the frame with the sample, and reducing the heating of the sample by the heat of polymerization (maximum 90 °C). A disadvantage is the cost of purchasing the necessary polymerization instrument with blue light (Technotray CU). This embedding system was developed for grinding techniques. It is therefore relatively hard but it can be mixed with other acrylic acid derivatives thus modifying the hardness.

For demanding cross-sectional investigations on samples which cannot be cut or which contain fibre types which break randomly when cut, grinding and polishing machines as used in materials analysis (for example metals, ceramics) are required.

8.4.3   Chromatography, preferably thin layer chromatography

Chromatography comprises an important group of separation methods in which mixtures of substances are separated into their components using a mobile and a stationary phase. With textile damage analysis the possibility of identifying the separated substances by comparing them with authentic samples is often as important as the separation itself. This identification is successful when the separation behaviour in one or, preferably, more separation systems is the same and when additional findings such as the same staining or reaction behaviour show that the substances are identical. A prerequisite for such chromatographic identification is that the identity of the substance is already suspected so that the relevant substances can be chromatographed at the same time for comparison. An even more fundamental prerequisite is that the substances to be analysed are soluble in the mobile phase. Naturally it is also important that a suitable separation system is known or can be developed.

Of the many chromatographic methods used in analysis the one preferably used in textile damage analysis is thin-layer chromatography (TLC). The reason for this is that TLC delivers results quickly, simply and cheaply, with usually sufficient accuracy for elucidation of damage cases. Dyestuffs, optical brighteners, soluble textile auxiliaries and fibre finishes are especially suitable for TLC. Many pigments are also sufficiently soluble. Cross-linked finishes, fibres, coatings and other polymers are unsuitable. For the analysis of these insoluble or polymeric substances the more costly pyrolysis gas chromatography (P-GC) and variations of high-performance liquid chromatography (HPLC) or, often simpler in the case of almost homogeneous polymers, infrared spectroscopy can be used.

The procedure in TLC consists of:

• depositing the samples on the starting line of the TLC plate
• chromatographical separation, also known as development

- detection of the spots if they are not already visible due to their colour
- evaluation and documentation.

All these steps are also available in an automated form, which can be advantageous for routine investigations. If a very high degree of separation is required high-performance TLC can be used (HPTLC). Here the layers have smaller grains with a narrower distribution of grain size (for example 5 μm instead of the conventional 12–20 μm). On account of their higher separation performance HPTLC plates are usually smaller (5 × 5 cm). The use of horizontal separation chambers further shortens the time for their chromatographic development.

   The extensive literature makes it easier to find suitable separation systems (coating of the plate and eluent) and to visualize colourless spots, usually with colouring reagents or by derivatizing to coloured compounds. Classical books on TLC have been written by Stahl,[65] Randerath[66] and Kirchner.[67] Newer books have been written by Nyderi[68] and Fried and Sherma.[69] There have been many publications on TLC of textile dyes (for example Rettie and Haynes[70] and Anonymous[71]). Schweppe gave a detailed description of TLC of dyes, pigments and optical brighteners.[72] An interesting sideline to damage analysis is detection with TLC as a rapid preliminary test of textiles in relation to their content of dyes which can be cleaved to carcinogenic aromatic amines.[73]

   TLC is particularly useful for analysing cases of damage caused by soluble stains or oily or greasy soiling. The following examples serve to illustrate this.

1. Identification of grease and oil stains is by means of TLC of hexane extraction residues of the stains in comparison to similarly sized samples without stains, and mineral oils and oleine,[74, 75] (see also Section 8.6.1):
   - stationary phase: ready-made TLC plates with Silica Gel 60 F 254 (Merck)
   - mobile phase: (a) *n*-hexane or (b) *n*-hexane/diethyl ether/glacial acetic acid 80:20:1 by volume
   - detection by molybdatophosphoric acid or anisaldehyde
   - mineral oil Rf value in eluent (a) 0.67 and in (b) 0.78
   - oleine Rf value in eluent (a) 0 and in (b) 0.12 with tailing to the start
   - many machine oils fluoresce in UV light.[43] This can more easily be seen with oil stains when the residue of the extract is tested in UV light (concentration of the oil).
2. TLC of carriers for polyester:[74, 75]
   - stationary phase: ready-made plates with Silica Gel 60 F 254 (Merck)
   - mobile phase: *n*-hexane/diethyl ether/glacial acetic acid 80:20:1 by volume
   - detection by UV light (254 nm) or, in the case of phenolic compounds, by 2,6-dichloroquinone chlorimide (1% solution in ethanol = spray solution A; spray solution B = 10 g anhydrous sodium carbonate dissolved in 60 ml distilled water and 30 ml methanol. After spraying with A and before spraying with B the TLC plate is dried with cold air from a hair dryer).
   - The Rf values of some authentic substances (phthalic acid dimethyl ester 0.1;

o-phenylphenol 0.2; biphenyl 0.6; benzoic acid phenyl ester 0.45) demonstrate the broad separation possible with this TLC method.

3. Polyester oligomers are a frequent cause of faults. They can be identified by TLC in comparison with authentic oligomers. Their detection by means of melting point determination and IR spectroscopy will be discussed in Section 8.5.5. Authentic oligomers can be readily obtained by extracting polyester with methylene chloride (which dissolves the core oligomers), dioxane or perchloroethylene. It is recommended that polyester goods should be cleaned first with petroleum ether and acetone and that the oligomers be recrystallized from boiling dioxane. Kobayashi has named several TLC systems for their analysis,[76] see also Lang and Makart.[77] A further method based on a TLC system that is also usable for disperse dyes is as follows:[78]

   • stationary phase: ready-made plates with Silica Gel 60 F 254 (Merck)
   • mobile phase: toluene/glacial acetic acid 9:1 by volume
   • detection by UV light and/or with Dragendorff reagent as a blue coloration obtained from barium bismuth iodide, Rf 0.8 (depending on purity with tailing to 0.3)
   • Preparation of the reagent: solution A = 1.7 g basic bismuth nitrate dissolved warm in 20 ml glacial acetic acid and 80 ml distilled water; solution B = 40 g potassium iodide in 100 ml distilled water; Dragendorff reagent is prepared freshly before using by mixing these solutions A and B, adding 200 ml glacial acetic acid and then distilled water to make 1 l. The spray solution is made freshly by combining two parts by volume of this solution with one part by volume of 20% barium chloride solution.

Many low-molecular weight textile auxiliary agents can be analysed with TLC and this can be useful in elucidating certain cases of damage. Known examples are stains caused by carriers or softeners. Cross-linking agents for cellulose, as used in easy-care finishes, can be identified by TLC after degradation with dimedone. Surfactants can be separated using TLC and identified by comparison with authentic surfactant.[79, 80] When mixtures of surfactants with different ionic forms are present it is recommended that they be separated first with an ion exchanger. Ethoxylated products can be separated by TLC into the individual species up to an ethoxylation degree of 20 to 25. This results in an impressive row of spots like a pearl necklace and the size of the spots gives a rough idea of the distribution of the degrees of ethoxylation.[81–83]

• stationary phase: ready-made plates with Silica Gel 60 F 254 (Merck)
• mobile phase: butanone/distilled water 50:50 by volume
• detection: Dragendorff reagent, then vapourized with iodine.

8.4.4   IR spectroscopy

Infrared spectroscopy (IRS) is often a useful supplement to TLC especially in the

analysis of insoluble or macromolecular substances. However, with mixtures of substances the superimposed IR spectra are often so complex that they can hardly be interpreted. A previous separation, including that with TLC, is very useful for IRS. Several books on IRS can be recommended.[84–86]

Molecules can be excited by absorption of IR rays to give stretching vibrations (in the direction of the bond) and also the somewhat less energetic bending vibrations with three or more atoms in the molecule. Thus as a rule spectra with many bands and containing a high degree of information are formed. The position and the shape of the IR bands are characteristic of the particular molecular structure which has been excited. IRS in the intermediate IR range from 2.5–25 μm, corresponding to 4000–400 cm^{-1} (wavenumber) enables the identification of functional groups and other structural parts of molecules. It can also be used for testing identity. If all the essential bands in the IR spectra of the sample and the authentic substance correspond, including those in the so-called fingerprint range of carbon backbone vibrations at about 1500–1000 cm^{-1}, the two substances are identical.

This shows that IRS is a particularly powerful method for damage analysis. With this method fibres, coatings and other deposits, textile auxiliaries and substances causing stains can be identified. Chemical damage to fibres can also be detected by means of specific structural changes. All states of matter can be investigated with IR spectroscopy. Thus in damage analysis the composition of mostly liquid extraction residues is of particular interest. As well as qualitative IRS, quantitative applications are also available, where on the basis of the Lambert–Beer law the determination of the concentration of dissolved substances, the blend ratio in fibre mixtures or estimation of the comonomer content in copolymers is possible.

On account of its high energy flow and favourable signal-to-noise ratio, modern Fourier transform IRS (FT-IRS) enables the use of very low energy analysis methods such as IR microscopy[87] and many interesting reflection methods including directed and diffuse reflection as well as attenuated total reflection (ATR). With the ATR technique the methods suitable for solids and liquids, namely horizontal multiple reflection and single reflection diamond ATR, are of particular interest. The advantages and disadvantages of the different IR sampling and measuring techniques suitable for textile applications, especially for damage analysis, can be found in the literature.[4, 88, 89]

The following examples serve to give an idea of the many possiblities for the use of IRS in investigating damage to textiles. The identification of fibres, including unwanted foreign fibres, of coatings, stains and other fibre deposits are the applications which spring most easily to mind.

The IR spectra of polyester oligomers are almost identical to those of polyester fibres. The oligomers can be prepared as KBr pellets, as a molten film between NaCl or KBr platelets or else they can be investigated directly by the diffuse reflection or the diamond ATR method.

Silicone stains still occur quite often and with the aid of IRS they can be readily

Table 8.5 Suitability of IR bands for identifying silicone stains, depending on the type of fibre[3]

Wave number (cm^{-1})	Cotton	Viscose	Wool	Nylon 6,6	Polyester
770–800	++	++	++	++	0 (+)
1020–1120	–	–	+	+	–
1260	+	+	0 (+)	–	–
2965	0 (+)	0	–	–	0 (+)

Explanation of symbols: ++ indicates very good suitability (single, non-overlapping bands); + good suitability; 0 means that because of superimposition silicone can only be detected by the markedly higher intensity of the bands; – means that no increase in intensity of the superimposed bands is recognizable.

and fairly sensitively detected by means of the Si–CH$_3$ rocking band at 800 cm^{-1}, several intensive Si–O–Si bands in the range from 1020–1120 cm^{-1} and Si–CH$_3$ bending vibrations at 1260 cm^{-1}. Table 8.5 lists the suitability of these bands for the detection of silicones depending on their superimposition with fibre bands.[3] Other types of stains such as paraffins, sizes, softeners and carriers are somewhat more difficult to identify by IRS.[3] On account of the intensive F–C main bands at 1200 and 1150 cm^{-1} fluorocarbon finishes can be detected by IRS at application levels of fluorocarbon polymer from about 0.3–1.2%, depending on the overlapping with fibre bands.[4] When dealing with complaints or analysing competitor's samples concerning bonded nonwovens the composition of the binder is of interest as well as the type of fibre. The binder can also be determined by IRS.[90]

Weber-Kälin[75] has given further examples that show how IRS can be used to elucidate cases of damage caused by stains:

- Very small stains on cotton were shown to be the carboxylate of an organic acid, partly on account of bands at 1550 cm^{-1}.
- Light stains on a wool fabric were identified as a mixture of mineral oil (using TLC) and fatty acid ethanolamide (using IRS). Such mixtures are used as antifoaming agents.
- Small fluorescent spots on a white polyester/cotton fabric were extracted and compared with extracts from samples without spots. With the aid of TLC and IRS the spots were shown to be a mixture of silicone and a disperse optical brightener.
- Tiny spots on cotton were shown by comparative IRS to be the calcium salt of polyacrylic acid.
- IRS on other small spots suggested after searching in an IR spectra library the presence of silicic acid, which could be confirmed by classical analytical chemistry (alkaline melt, yellow precipitate with ammonium molybdate after exclusion of silicone).[7]

Self-collected or purchased IR spectra libraries[91–94] are very useful for the identification of unknown substances. With computer-aided library searches a correspondence

of about 80% of the bands is often sufficient to obtain a first idea or working hypothesis. If several possible identity solutions are offered it is the discrepancy between the first suggestion and the next which is more important than the absolute degree of correspondence with the spectrum of the substance being sought after. If several suggestions are made with only a few per cent discrepancy between them, all of these substances should be included in the clarification of the damage.

8.4.5 Thermal analysis

Thermal analysis (TA) is the comprehensive name for a group of analytical methods in which physical or chemical properties of a sample are measured as a function of temperature and time. The sample, contained in a defined atmosphere (usually air or nitrogen), is subjected to a controlled temperature programme, for example it can be tested isothermically or with a constant rate of heating or cooling. TA has been indispensable in polymer technology and research for a long time. In the area of textiles it has increased in importance owing to the fast-growing market segment of technical textiles, for example in quality control and in analysis of products, competitor's samples and damage. In the other textile market segments, namely apparel and household textiles, TA is especially important in damage analysis.

A database research using the keywords textile and TA (including the methods DSC, TGA and TMA, which are explained below) showed a marked difference in their relevance for textiles. By far the most important is differential scanning calorimetry (DSC), followed by thermogravimetric analysis (TGA) and finally thermomechanical analysis (TMA). Several books can be recommended for further information on these methods.[95–97]

Determination of melting point

The determination of melting point as used for fibre identification can itself be included under TA, because here the phase change is determined as a function of temperature. It can be carried out very easily using a Kofler hot bench.[98] This has a temperature range from about 50–260 °C. Fibre snippets are moved with tweezers from the colder to the warmer end until they begin to melt. The relevant

Table 8.6 Temperature range for softening and melting of fibres, arranged in order of increasing melting point or decomposition temperature.

Type of fibre, chemical basis (trade names)	Softening range	Melting range
Polyethylene, PE (HD = high density)	105–120	**124–138 (up to 155)**
Polypropylene, isotactic, iPP	150–155	**160–165 (175)**
Polypropylene based on metallocene catalyst, more highly isotactic, **iPP(Mc)**		**147–158 (130–160)**
Polyoxymethylene, POM (Delrin, Tenac)		165

Polylactic acid, PLA (e.g. Ingeo, Lactron, Lacty, Lacea)		140–178
Poly(vinyl chloride), PVC	65–90	150–180 d
Poly(vinyl chloride) postchlorinated, PVC+	85–110	150–180 d
Poly(vinylidene chloride), PVDC	90–140	150–180 d
Polyamide 12, PA 12 (Grilamid)		172–175
Polyamide 11, PA 11 (Rilsan)		180–190
Polyamide 6.10, PA 6.10 (Brulon, Decalon, Platon, Survon)		214
Polyamide 6, Nylon 6, PA 6	170–200	**215–220**
Polyurea, PUA (Urylon)		216
Copolyester A-Tell (Polyesterether PEE)		218–219
Polystyrene, PS	70	218–220
Polyglycolic acid, PGA (Merilon)		215–223
Poly(butylene terephthalate), PBT (e.g. Trevira ESP, Nylstar Elite)		221–225
Poly(trimethylene terephthalate), PTT (e.g. Corterra, Solo, Solona)		228
Copolyester Grilene, PES(G) (Polyesterether PEE)		229
Polyvinylalcohol, PVA		232
Copolyester Vycron, PES(V) (Comonomer isophthalic acid)		237
Polyurea Urylon, PUA		237
Polyacrylonitrile, PAN or **PAC**	190–250	from **260–270 d**
Elastane (e.g. Lycra, Dorlastan), **PUR(E)** or **PUE**	170–210	**230–260**
Diacetate, CA		**255–260 d**
Polycarbonate, PC		245–256 (150–300)
Polyester normal type, PES(N) or **PET**	230–240	**254–256 (250–260)**
Polyamide 6.6, Nylon 6,6, PA 6.6	220–235	**255–260**
Polyamide 4, PA 4 (Taimir)		256–265
Poly(ethylene naphthalate), PEN		270
Qiana (alicyclic polyamide)		270–275
Poly(dimethylcyclohexane terephthalate), Kodel, Vestan, PES(K),	260–265	282/295
Triacetate, CT		**290–300 d**
Basofil (Melamine-formaldehyde-polycondensate)	> 220 (d)	330–350 d
Kynol (Phenol-formaldehyde-polycondensate)	230 (d)	350 d
Polyetherketone, PEK, also PEEK (e.g Zyex)	> 250	324–366
m-Aramid, *m*-AR, PMPIA (e.g. Nomex, Conex)	320	370 d
Polyamideimide, PAI (Kermel)		380–400 d
Polytetrafluoroethylene, PTFE (Teflon)	330 (d)	410 d
p-Aramid, *p*-AR, PPTA (e.g. Kevlar, Twaron)		425–500 d
Polyimide, PI (P84)	> 260	> 500 d
Poly-*p*-phenylene-2,6-benzoxazol, PBO (Zylon)		650 d
Polybenzimidazol, PBI		660 d

Approximate values in °C (d = decomposition). Standard fibres emphasized.

temperature is then read off a scale which has to be previously calibrated. In this way the melting point or melting range can be determined in a few minutes with an accuracy of about ±2 °. As the melting points for fibres given in Table 8.6 show, this accuracy is usually sufficient for fibre identification. With intimate fibre blends a melting point or hot stage microscope is necessary. This has a heated microscope stage as well as a simple polarizer and analyser. Since the crystalline structure of the fibres collapses on melting the melting point can be determined very exactly in polarized light because the interference colours seen here, arising from the crystalline structure, disappear as soon as the fibre melts. In this way the melting point can be determined with an accuracy of ±0.5 °. However, during the last 5–10 ° before melting, the heating must take place very slowly (2–3 ° min^{-1}) in order for optimal transfer of heat from the stage to the fibre sample to be assured. If heating takes place too rapidly the melting point obtained is too high. An advantage of the hot stage microscope is that in fibre blends the melting behaviour of all the fibres can be observed consecutively. Even if a fibre does not melt when heated up to 300 °C, for example, this can still be a useful piece of evidence for its identification.

Differential scanning calorimetry (DSC)

Using DSC the temperature range for melting (T_m) or for decomposition (T_d) and, during cooling, that of crystallization (T_c) can be determined along with the corresponding enthalpies (heat of fusion H_m, heat of decomposition H_d and heat of crystallization H_c). Furthermore the characteristic temperature for the amorphous areas, the glass temperature (T_g) and the so-called effective temperature or middle endotherm peak temperature (MEPT) can be determined. By comparing the measured heat of fusion with the theoretical value, the purity or content can be determined. This is particularly relevant for fibre recycling. Similarly the measured heat of reaction can be compared with the theoretical value in order to calculate the extent of reaction, for example with cross-linking reactions.

For damage analysis of textiles made from polyester the MEPT is especially interesting because it gives insight into the thermal prehistory of the fibres.[99–101] The MEPT is the maximum temperature of a small endothermic peak between the small endothermic stage of glass transition and the large endothermic melting peak. The position of this MEPT peak is variable and depends on the temperature of thermal pretreatments (T_p). Its size depends on the intensity, and thus mainly on the duration of the thermal treatment and also on the tension, for example during setting. The measured MEPT usually lies several degrees above the temperature of a preceeding thermal treatment (MEPT > T_p). It gives useful information for damage analysis. For example, it is possible to determine from this temperature whether polyester goods were dyed at the boil (with carrier), under high-temperature (HT) conditions or using the thermosol process. Conclusions about setting temperature are also possible, in particular differences in setting conditions

can be determined exactly. Unfortunately, this thermal memory also has notable restrictions. It can be superimposed by mechanical influences; for example differences in tension also affect the MEPT. The way in which the heat was applied (steam, hot air, conducted heat) also causes significant differences. Finally, a strong thermal influence should not have taken place subsequently as this extinguishes the memory of the weaker influence.

The model of Jeziorny[102] to explain the phenomenon of MEPT helps to make these factors understandable. According to this model, small increasingly ordered areas, the so-called microcrystals, are formed under increased heat input from initially unordered structures on the surface of the crystalline areas of the fibre. These then melt during the DSC measurement. If the sample is cooled after the first DSC measurement and then subjected to a second run, a MEPT peak is no longer found. Comparing the first and second run thus makes it easier to find and interpret this thermal event. If the DSC instrument is sufficiently sensitive a MEPT peak can also be found with nylon fibres. Its allocation to thermal pretreatments is, however, more difficult than with polyester because, among other reasons, the rate of crystallization is higher for nylon.

DSC is also useful for characterizing bicomponent fibres, film-forming finishes and coatings. For example, with polysiloxane a very low glass temperature (about $-120 °C$) is characteristic, followed by a crystallization peak (at about $-100 °C$) and a large melting peak ($-40 °C$). As a matter of interest the enthalpies obtained by integration of these peak areas enable the crystalline ratio to be calculated: $(H_m - H_c):H_m$. This calculation is also possible with polyester, especially with granules, on account of their higher amorphous content. Fischer has described a relation between the glass temperature of film-forming finishing agents and the hardness or softness of the corresponding finishes.[103]

Thermogravimetric analysis (TGA)

With TGA the change in weight of the samples on heating is determined (usually possible up to 1000 °C). In a nitrogen atmosphere the decomposition of the sample can thus be studied; in air the ability to be oxidized is additionally determined. In this way fibres modified to be flame-resistant can be distinguished from standard fibres. In fibre composites, for example fibre-reinforced rubber, it is thus possible to determine the proportions of the components with relatively little effort: moisture and softeners in the first stage of weight loss up to about 220 °C, then the fibre and rubber components up to 500 °C and finally after changing from a nitrogen atmosphere to air the carbon used as a filling burns and above 700 °C the non-burnable inorganic filling remains. The first derivative of the weight loss curve, the derivative TG (DTG), enables a more exact determination. By coupling TGA with a mass spectrometer or a FT-IR spectrometer the decomposition products can be analysed. Because of the higher costs such methods are only used in exceptional cases for textile damage analysis.

Thermomechanical analysis (TMA)

Thermomechanical analysis (TMA) investigates the changes in the dimensions of a sample as a function of the temperature, for example shrinkage or extension of fibres.[104] It is easier to work here with filaments than with staple fibres. Fibre composites and other materials are also analysed by dynamic loading. This dynamic mechanical analysis (DMA) enables, for example, the glass temperature of elastomers to be determined exactly. But in textile damage analysis TMA is seldom used.

In conclusion the most important advantages and disadvantages of thermoanalytic methods, both in general and in textile damage analysis, can be summarized:

- variety of applications and sophisticated instruments
- information about the thermal prehistory of polyester
- small quantities of sample are sufficient (about 5 to 10 mg)
- difficulties in obtaining representative samples
- the sample is usually damaged or destroyed by the heat (important for example in forensic applications, see Section 8.7.1)
- danger of misinterpretation of the results (correct allocation of the thermal events is made easier by simultaneous TA, for example DSC and TGA simultaneously).

8.4.6   Further methods

There are a large number and variety of methods which can be used for damage analysis of textiles and these methods can naturally also be combined. It is economic restraint which most affects the imagination of the damage analyst. In other words, any method can be considered for damage analysis if it is or could be useful, does not cost too much and does not take too long.

In addition to the important methods of damage analysis described above three further methods will be briefly described here.

Techniques for surface immprints

Imprint techniques have been a proven and important method in damage analysis of textiles for a long period of time. It is often advantageous not to investigate the original object under the microscope but rather the negative imprint of its surface:

- In an imprint it is often possible to see if a fault in a coloured textile was caused during textile manufacture or during dyeing and finishing. Spinning faults, such as use of different fibre counts or differences in yarn twist, and faults in fabric production can be seen in the imprint as well as in the original (and in the same location). On the other hand, faults arising from dyeing or printing are eliminated in the imprint.
- The imprint is transparent and the colour of the sample does not interfere. Thus

Table 8.7 Comparison of the advantages of the most important surface imprint methods

Imprint with gelatine-coated plates	Imprint with thermoplastic films
No thermal influence on the sample No special equipment necessary	No swelling of hydrophilic fibres With a commercial instrument[107] larger areas (approximately 20 x 30 cm) can also be tested
No false indication of structural differences, arising from diffusion of grease, oil or wax deposits (possible effect on films)	Detection of grease, oil or wax deposits possible due to diffusion into and dulling of the film

with dark-dyed wool fibres the cuticle scales can only be easily recognized in the imprint. The same applies to abraded places and other types of mechanical damage to the surface of dark dyeings.

- Since the surface imprint is very thin (about 0.02 mm) the depth of focus is usually much better than in direct microscopy of the uneven, three-dimensional textile surface and possible fibre lustre and transparency do not interfere. In direct microscopy with reflected light the image is usually not sharp because the fibre interior and the underside of the fibre also reflect light.
- Since the transparent imprints are examined in transmitted light, it is not necessary to have a microscope with reflected light. In addition, the original sample remains unchanged.

There are two different widely used imprint methods in damage analysis, namely imprints on gelatine-coated plates[105] and on thermoplastic films, usually polypropylene or polystyrene.[5, 106] In Table 8.7 the most important advantages of these complementary imprint methods are compared.

Principle of the method with gelatine-coated plates

Two grams of gelatine are swollen in 40 ml of distilled water for 1 h at about 35 °C. One part of this swollen gelatine is diluted with three parts distilled water, and 10–20 ml of this solution are sufficient for about 100 cm² of glass plate surface. The solution is brought evenly onto clean glass plates, for example microscope slides, with a pipette. After drying for 24 h in a dust-free place the plates are ready for storage or use. Before use they are dipped briefly into water and the adherent water then removed by shaking. The fabric is then laid on the swollen gelatine and covered with a filter paper and a further glass or metal plate. A weight is added, which should cover the upper plate evenly. For glass plates that are the same size as microscope slides the weight should be about 500 g. After pressing for 30 min the textile side is dried briefly with a warm hair dryer and then carefully removed from the imprint. Further details can be found in the publications by Bigler[105] and

Peter,[24] who was able to obtain structured shadows (pseudo stereo effect) by displacing the condensor sideways (oblique transmitted light).

Principle of surface imprints with thermoplastic films

The thickness of the films (usually with polypropylene 30–40 μm, or with polystyrene 100–200 μm) depends on the thickness of the individual fibres and yarns or the structure of the fabric. Polystyrene films are preferred for large-scale imprints (up to about 20 × 30 cm) in the Streak Analyzer.[107] For small-scale imprints a piece of film cut to a suitable size is pressed firmly together with the textile sample between two polished metal plates, for example in the size of microscope slides, with two screw clamps. The assembly is placed in a drying oven at 105 °C, in the case of polypropylene for 30 min and with polystyrene for 45 min. After cooling as rapidly as possible with cold air the sample is separated from the film. The film can then be examined in transmitted light in the microscope without the use of embedding agent. Further details are given by Mahall.[5, 106]

Extraction methods

A typical textile laboratory is characterized by several Soxhlet extractors standing in the fume cupboard. That is to say, the extraction of textile samples is a routine or standard procedure. During extraction, substances soluble in organic solvents or water are removed from the textile, then, as a rule, concentrated by distillation and the extraction residue is analysed qualitatively and/or quantitatively. Examples of extracted substances are stains, fibre spin finishes, lubricants, residual grease in wool, residues of surfactants and other chemicals such as acids, bases or thickeners, soluble finishes, dyes and optical brighteners, pesticides and other biocides, carriers, heavy metal salts and formaldehyde. Stepwise extraction using solvents of increasing polarity (for example first hexane, then methylene chloride, then absolute alcohol and finally water) can give a first indication of the nature of the extracted substances.

   Different extraction methods and apparatus can be used. Some of the procedures are standardized.[108] Mini versions of the Soxhlet extractor are prefered for very small samples such as stains. As alternatives to the Soxhlet extractor, automated apparatus have been developed. The Morapex rapid extractor[109, 110] enables the test sample to be extracted non-destructively in a very short time with either water or organic solvents.

Average degree of polymerization of fibres

Many types of damage, including chemical, thermal, photolytical, biological and some types of mechanical damage, are based on degradation of the polymer chains in the fibre. Thus determination of the average degree of polymerization (DP)

gives a direct scale for assessing the extent of such damage but not its cause. The time and cost of determining DP is, however, so great that, whenever possible, simpler but less accurate methods are preferred. Examples of these are loss of tensile strength and abrasion resistance or the pinhead reaction with cotton (see Section 8.5.1). An advantage of DP determination is that it allows quantitative estimation of the damage. For example, Eisenhut[111] defined a damage factor *s* for cellulose fibres based on the decrease in DP, which allows comparative assessment of damage for cotton and regenerated cellulose fibres:

$$s = \log \left[(2000 : P_1) - (2000 : P_2) + 1 \right] : \log 2$$

where P_1 = DP before damage and P_2 = DP after damage.

Damage factors of $s < 0.5$ are said to be acceptable after bleaching treatments, but with $s > 0.75$ the goods are said to be badly damaged. It must be borne in mind that the damage factors are also dependent on the method used, they are higher with the cuoxam method than with the EWNN method.[112]

Of the many methods known for determining DP, measurement of viscosity according to Staudinger is the one preferred in damage analysis because it can be carried out in any textile laboratory. The viscosity is measured indirectly via the times taken for the polymer solution and the solvent to run through an Ubbelohde or Ostwald viscosimeter. A prerequisite is that a suitable solvent is available for the fibre and that the corresponding constants for the calculation are available. The solvent must not damage the fibres and it should be easy to handle. Sometimes, however, health-damaging m-cresol has to be used (polyester, nylon). Schefer[113] has listed solvents and viscosity constants for 16 undamaged fibre types.

In order to give an idea of the other methods which are used for damage analysis[7, 5] the following examples are listed:

- detection of metals, such as Fe, Cu, Ca, Mg, and non-metals, such as N, P, S, Cl, F, which can help to elucidate the damage
- swelling and solubility tests, especially, but not only, with natural fibres
- determination of concentration, for example by means of titration, gravimetry or colorimetry
- staining tests which mark, for example, setting differences, oil and grease deposits or fungi. They generally have the disadvantage that the samples have to be undyed or only lightly dyed. It is time-consuming if the original dyeing first has to be removed in order for staining with test dyes to be carried out and there is also the danger that additional damage may occur during stripping of the dyeing.

Instead of describing these methods here for the general case it would appear more suitable to discuss them in relation to the type of fibre involved in the damage. This is covered in the next section.

Choice of the most suitable method is made more difficult if there is very little sample material available. An ideal method should be highly sensitive,

reproducible and give clear-cut results. A common combination of methods, especially when analysing stains, begins with microscopy, followed by concentration after extraction. The extract from an undamaged area serves for comparison. For identification the preferred methods are TLC (if authentic samples are available for comparison) and IR spectroscopy. Reference spectra are also very useful here but it is possible to identify the substances causing damage by direct interpretation of the spectra.

8.5   Damage analysis according to the type of fibre

The extensive subject of damage analysis of textiles can be divided into typical cases of damage depending on the stage of processing or the technology of yarn and fabric production such as:

- filaments, threads and yarns[114, 115]
- woven fabrics[116]
- knitted fabrics[117–120]
- nonwovens
- textile composites, coated fabrics.

An additional type of damage occurs during cleaning operations, such as washing[121] and dry cleaning. Although this division may be useful for many typical types of faults, a division according to the type of fibre appears even more suitable. In this way the types of damage typical for a particular fibre can be meaningfully grouped. For example, cellulosic, protein and synthetic fibres each have their own characteristic strengths and weaknesses, which are enlightening when analysing damage to them. In the following section the most important methods of damage analysis will be described for the respective types of fibre.

8.5.1   Damage analysis of cellulosics, especially cotton

In contrast to wool, cellulosic fibres are relatively stable to alkali but sensitive to acid. In addition, cellulosic fibres can be damaged by strong oxidizing agents, excessively high temperatures and microorganisms. The extent of this damage (the damage factor) can, among other means, be assessed by viscosimetric determination of the degree of polymerization, as described in Section 8.4.6. A much easier method is the following reaction.

'Pinhead' reaction with cotton[122, 123]

This rapid microscopic test indicates chemical damage to cotton and enables the degree of damage to be roughly estimated. The cotton fibre to be tested is cut with very sharp scissors or a razor blade to snippets of about 1 mm length and embedded with 15% sodium hydroxide on a glass slide. After covering the sample with a

Table 8.8 'Pinhead' reaction and damage to cotton[122, 24]

Type	Formation of pinheads	DP range
1 Undamaged	Well-rounded pinheads on about ¾ of all fibre snippets	> 1500
2 Clearly damaged	Mostly flat protuberances with some semi-rounded pinheads	1600–1000
3 Heavily damaged	Cut ends mostly flat with some flat protuberances	1100–700
4 Very heavily damaged	All cut ends smooth with varying width of lumen, fibres partially convoluted	800–400
5 Extremely damaged	Surface notches, longitudinal and transverse splits, fibrillation and marked deformation	< 400

DP = average degree of polymerization

cover slip and leaving for 2–3 min the formation of 'pinheads' at the cut ends is evaluated. In Table 8.8 the appearance of the 'pinheads' is described corresponding to different stages of damage and approximate ranges of the degree of polymerization.[24, 122] In undamaged cotton the primary wall surrounding the secondary wall is intact so that the cellulose in the secondary wall, which swells strongly in sodium hydroxide, is pressed out at the cut ends and thus forms the pinhead shapes. After chemical damage to the primary wall the fibre can swell laterally without restriction and thus does not form pinheads. This 'pinhead' reaction is said to be applicable to cotton after every stage of processing and finishing but it does not work with flax or ramie.[122] Cotton which has been given easy-care properties with cross-linking agents only swells slightly and thus does not show any marked pinheads. This can suggest a higher degree of chemical damage than is actually present. Since more than 90% of cross-linking agents for cellulose contain formaldehyde the results of the pinhead reaction should be confirmed by testing for formaldehyde with chromotropic acid: a small sample of fibres is heated carefully to a maximum of 100 °C in 1–2 ml of 72% sulphuric acid in which a little chromotropic acid is dissolved (about 10 mg in 100 ml). The formation of a reddish-violet colour after 1–2 min indicates the presence of formaldehyde.

If the pinhead reaction demonstrates chemical damage the next point of interest is to determine the exact cause. The tests described below for damage caused by chemicals or fungi are applicable to all cellulosic fibres.

Detection of acid damage with Fehling's solution

Since cellulosic fibres are sensitive to acids they can be easily damaged by the acid catalysts used in easy-care, silicone, fluorocarbon and flame-retardant finishes as well as by drops of concentrated acid or faulty dyeing of cellulose/wool blends.

Carbonization of wool is based on this sensitivity of cellulose to acid. Acid damage is also known to occur in sulphur dyeing (cleavage of sulphuric acid during storage) and in contact between cellulose textiles with easy-care finishes and chlorinated bathing water or detergents containing chlorine bleach (chloroamines are formed, which decompose to hydrochloric acid and oxygen).

The 1,4-glucosidic bonds in the cellulose chains are cleaved hydrolytically by acids. Cellulose damaged in this way, so-called hydrocellulose, is characterized by the shorter length of the molecules and thus a higher concentration of end groups. One end of the chain has a ring-forming hemiacetal structure in equilibrium with the open-chain aldehyde form. This chemical test for damage is based on the higher concentration of aldehyde groups after acid cleavage.

Fehling's solution is prepared freshly by mixing equal amounts of Fehling's solution A and B (A = 6% copper sulphate solution, B = 20 g of sodium potassium tartrate and 10 g of sodium hydroxide in 100 ml distilled water) and diluting with an equal amount of distilled water. The sample, which was previously degreased and soaped at the boil, is boiled in this test solution for 5 min, during which it is kept below the liquid level and prevented from contact with air by means of a glass rod. If this is not done, an interfering green colour occurs. After rinsing with water and very dilute acetic acid the formation of a red colour due to precipitated copper (I) oxide indicates acid damage. In principle during this redox reaction the aldehyde groups of the cellulose chains are oxidized to carboxylic acid groups and the copper is reduced from copper (II) to copper (I). It is important here to compare with acid-damaged reference samples and undamaged goods, since the latter also show a slight red coloration. The aldehyde groups may already have been partially oxidized by atmospheric oxygen. Only a marked red coloration is a sure sign of acid damage. In cases of doubt this test should be repeated. The following reverse conclusion may also be useful here: if the pinhead reaction indicates chemical damage and the oxycarmine test described below is negative, there is a high probability that acid damage has occurred.

The detection of aldehyde groups with ammoniacal silver solution, as recommended in the literature,[7, 124] is dangerous because the reagent can explode after standing for longer periods.

Detection of oxidative damage with oxycarmine

Cellulosic fibres are often oxidatively damaged when the most commonly used bleaching agent, namely hydrogen peroxide, decomposes catalytically. This unwanted decomposition to aggressive radicals is catalysed especially by heavy metals. Traces of iron (abraded metal, rust from water or steam pipes), for example, are sufficient to cause severe catalytic damage during peroxide bleaching. The damage is manifested as a marked loss of strength or even formation of holes. Naturally, it is difficult to detect traces of iron around the edge of these holes. This will be discussed in the next section.

Oxidatively damaged cellulose, known as oxycellulose, is characterized by polymer chain degradation and an increased concentration of carboxylic acid groups. These arise not only from the aldehyde groups at the end of the chains, such as described for hydrocellulose, but also to a much larger extent from the primary alcohol groups of the C-6 atoms of the many β-glucose constitutional elements. These primary alcohol groups are fairly readily accessible. They can thus be easily oxidized to carboxylic acids via the aldehyde intermediates. Under strongly oxidizing conditions the secondary alcohol groups of the C–2 and C–3 atoms can be oxidized to keto structures, which after cleavage of the bond between the C–2 and C–3 atom also form carboxylic acid groups.

These numerous carboxylic acid groups, distributed along the cellulose molecule, are the basis for the chemical detection of oxidative damage. As a rule this detection is more intensive and unequivocal than that for acid damage with Fehling's solution, which is based only on the end groups. The carboxylic acid groups formed by oxidation bind basic dyes via salt links, whereas these dyes do not stain undamaged cellulose. A well-known example is the staining test with Methylene Blue:[125] the sample is stained with a 0.1% aqueous Methylene Blue solution either cold for 20 min or at 60–100 °C for 5 min and then thoroughly rinsed. Staining with the test dye oxycarmine[126] is said to be four times as sensitive as with Methylene Blue[123] and is specific for oxycellulose. The test dye has to be freshly prepared from two storeable components and can only be used for one day. The dyeing conditions are simple and explained in the product information. It is also important here to have comparative stainings on undamaged and oxidatively damaged goods in order to interpret the blue coloration correctly.

Catalytic damage and detection of iron

Typical evidence of catalytic damage is a local marked loss of strength and often tiny holes, where the cellulose has been so severely destroyed by oxidation that it has been dissolved out of the fabric. In the case of dyed fabrics the edges of these holes are usually lighter coloured or colourless since oxycellulose has a decreased affinity for the usual cellulose dyes. In fabrics with optical brighteners a decreased or quenched fluorescence in UV light may be observed around the holes; areas containing metal appear darker. The edges of the holes are dyed intensively blue with oxycarmine. In the case of cotton the severe chemical damage in these areas is indicated by the lack of formation of pinheads in the corresponding test. These detection reactions become more difficult if the edges of the holes have been broken off by mechanical stresses during bleaching, dyeing or scouring. In spite of this, additional tests for traces of metals such as iron or copper should be made. Although all the heavy metals catalyse the decomposition of hydrogen peroxide, iron is most often involved.[127] Detection of other metals has been described by Agster.[7]

Iron can be detected on the fabric as well as in the combustion residue. The best-

known methods for detecting iron are with thiocyanate or as Prussian blue. In each case either the fabric is wetted at the relevant places with 1–2 drops of semi-concentrated analytical grade hydrochloric acid (10–15% or 6 N) or the combustion residue is dissolved in the porcelain crucible in 1–2 ml of this hydrochloric acid. After adding a few drops of ammonium or potassium thiocyanate solution (about 10%) an intensive red colour is formed. By adding a little diethyl ether to the solution in a test tube and shaking the colour can be concentrated in the ether phase. For detection in the form of Prussian blue a few drops of a 10% solution of tetrapotassium hexacyanoferrate solution are added to the acidified fabric or the solution. The fabric can also be tested by adding directly drops of a test solution consisting of 1 g of tetrapotassium hexacyanoferrate, 100 ml of 1 N hydrochloric acid p.a. and 50 ml of ethanol.[74] In the presence of ferric iron an intensively blue precipitate of $Fe_4[Fe(CN)_6]_3$ is formed. Schliefer and Heidemann[127] recommend the detection of iron as Prussian blue, which precipitates on the fabric within a narrow area and is not absorbed and distributed by the fibre capillaries, as is the case with soluble iron thiocyanate, which makes this detection method less sensitive. Also, in contrast to iron thiocyanate, Prussian blue is very stable. If technical grade hydrochloric acid is used instead of analytical grade a blank sample should be tested since traces of iron in technical hydrochloric acid can be falsely assigned to the fabric.

Mechanical damage

Mechanical damage can best be seen in longitudinal mounts under the microscope or in surface imprints. Since individual mechanically damaged fibres may not be representative of the sample, a fairly large number of fibre samples should be examined (up to 100 according to the particular case).

Damage by microorganisms

Cellulosic fibres are more often damaged by fungi than by bacteria. The microscopic detection of fungi will be described in more detail in Section 8.6.3. Storage of moist fabric overnight in a warm environment can be sufficient to cause fungal attack, leading to variously coloured mildew patches, which are difficult to remove.

Alkali spots

Cellulosic fibres, especially cotton, are pretreated with alkali. After rinsing off, a certain amount of residual alkali usually remains in the fabric and this is often distributed unevenly.[128] This can lead to faults in subsequent processes where alkali interferes, for example with acid-catalysed finishes (easy-care, water-, oil- and soil-repellent, stretch finish). Another problem caused by alkali is alkali spots,

usually caused by uneven addition of alkali (for example, splashes). The cellulose fibres swell more in these places and thus take up more dye, causing dark spots in the fabric. In undyed fabric alkali spots can occasionally be seen on account of their yellowish colour. The more markedly swollen fibres can be detected in an exact microscopic comparison of the longitudinal view of fibres from the spots and fibres from undamaged areas. According to Schmidt[40] the effect of the alkali can be recognized by a marked green coloration in the red/green test (dyed fabrics must be previously stripped of dye under gentle conditions). The red/green test is briefly described in a following section.

Differences in mercerization

During mercerizing, a treatment with concentrated sodium hydroxide under tension, the structure of the cotton fibre is irreversibly changed. The convolutions are removed and the cross-section becomes almost round. Dyeability, dimensional stability, handle and lustre of the fabric are improved. Since this process is influenced by many factors it is not surprising that differences in degree of mercerization, and thus complaints, can arise. Therefore the degree of mercerization is determined in order to express the quality of the mercerization. A comparison of suitable methods for this purpose was given by Hermanutz *et al.*[129] It is understandable that microscopical methods including image analysis have been developed to evaluate the degree of mercerization and the maturity of cotton. Examples can be found in the literature.[130–133] The assessment of the degree of mercerization is also possible with near-IR spectroscopy.[134] For damage analysis it usually suffices to carry out microscopic investigations, preferably on surface imprints, and in difficult cases also on cross-sections. Differences in tension during mercerization are a widespread cause of uneven dyeing. They can be detected by the red/green test (with increasing tension redder).[135]

Damage by heat and light (pyro- and photocellulose)

Cellulosic fibres are not particularly sensitive to heat and light. However, they do turn yellow after over-exposure to heat or light and lose strength owing to decomposition reactions. Pyrocellulose is said by Agster to show the reactions of both hydro- and oxycellulose.[136] Cotton damaged by light is said to react more like hydrocellulose whereas cellulose-regenerated fibres delustred with titanium dioxide are said to respond more to the reaction for oxycellulose after damage by light.[137]

Faulty quality in cotton, in particular neps from immature and dead cotton

Differences in fibre quality in one lot of cotton can lead to uneven fabric appearance. These differences cause higher costs in dyeing and finishing and represent a

difficult challenge for the dyer. They are also often the reason for customer complaints. Immature and dead cotton as well as the so-called hard or red cotton (with high concentrations of calcium or iron compounds) are not themselves typical forms of damage but are a frequent form of faulty quality with similar negative effects.

Calcium and iron compounds can be removed with weak acids or sequestering agents during pretreatment. Immature and dead cotton fibres have a secondary wall which is too thin and thus they have a low flexural rigidity. During processing these fibres entangle with each other and form so-called neps. Especially with dyed fabrics these pill-like entanglements often first become irritatingly noticeable after dyeing. They cannot be removed and lower the fabric quality. The annual losses thus caused were estimated in 1996 to be US$200 million for the US textile industry alone.[138] Covering of immature and dead fibres differs according to the dyestuff class and the individual dye. Problems with uneven fabric appearance occur especially with direct and vat dyes. Unfortunately, there is no textile auxiliary agent which solves this problem. The quality of immature cotton can, however, be greatly improved by mercerization. The treatment with caustic soda causes the relatively thin secondary walls of the immature fibres to swell. As with mature cotton, the fibre cross-section remains approximately circular after mercerizing and drying and the uptake of dye is improved. Dead cotton hairs have died off at an early stage of growth so that the secondary wall, if present at all, is very thin. Their cross-section is correspondingly flat. After mercerization they are said to be disadvantageously modified, their neps become flatter and reflect incident light even more than immature cotton, which swells more strongly. Light-coloured neps are one of the most frequent causes of complaint with cotton textiles.[120, 139]

There are many publications on the subject of neps and their detection, for example Furter and Frey,[140] and on the determination of the degree of maturity of cotton.[141, 142] Here, only the principle of the so-called red/green test will be briefly described, since it is easy to carry out in any textile laboratory[5, 7, 143] and it gives a quick idea of the proportion of immature cotton. It does not correlate well with other tests of maturity.[130–133, 144, 145] On the other hand, cotton samples which show the same degree of maturity after the usual maturity test with the air-flow method often show subsequent differences in depth of dyeing,[145] thus underlining the importance of this dyeing test.

The red/green test was introduced by Goldthwait, Smith and Barnett and is thus also known as the GSB test.[143] It was developed for raw cotton. However, Denter *et al.* recommend previous alkaline scouring.[145] When the red/green test is used on yarns and fabrics neps become more clearly visible as small green spots. Using a mixture of a red direct dye with small molecules and a green direct dye about twice as large (Table 8.9) the mature, thick-walled cotton fibres are dyed mostly red and the immature, thin-walled fibres, but also very fine mature fibres, are dyed mostly green. This effect is based on differences in substantivity, rates of diffusion and

Table 8.9 Commercial dyes for the red/green test

Colour Index	Direct Red 81	Direct Green 26
Literature references	Sirius Red 4 B (Bayer/DyStar) Solar Red B (Sandoz/Clariant) Diphenyl Red 5 BL (Ciba-Geigy) Diphenyl Red 5B 182% (Ciba-Geigy)	Sirius Light Fast Green B (Bayer/DyStar) Solar Brilliant Green BL (Sandoz/Clariant) Solophenyl Green BL (Ciba-Geigy)
Commercially available replacement dyes	Ciba Pergasol Red 2B 182% (Ciba SC) Levacell Red 5B liq. (Bayer, paper dye) Direct Red 81 (Aldrich)	Ciba Solphenyl Green BLE 155% (Ciba SC) Sirius Green S-4B (DyStar)

washing-off of these dyes and also on differences in the structure, accessibility, pores and affinity of the cotton fibres. It is of interest for damage analysis that the red/green test can also be used for the detection of differences in cotton caused by alkali treatment or mercerization[40, 135] (see the previous sub-section on alkali spots).

Swelling of regenerated cellulosic fibres in caustic soda

Reiter described the microscopic identification of regenerated cellulose fibres.[28] Kornreich[146] was able to distinguish between mechanical and chemical damage by means of a microscopic swelling test in 30% caustic soda. Damaged fibres and undamaged ones for comparison are placed next to each other on a microscope slide and covered with a cover slip. While the fibres are being observed, 30% caustic soda is drawn through the dry sample and the cover slip immediately pressed down evenly with a dissecting needle. Chemically damaged viscose fibres then break in a longitudinal direction or fall apart into fragments. Fibres which are not chemically damaged only show swelling, which recedes after the pressure is released.

   Further tests for damage on regenerated cellulosic fibres, such as iodine absorption, core/sheath differentiation, peeling methods, detection of traces of sulphur or copper as well as some hints for investigations on bast fibres are given in the literature.[147]

Diacetate and triacetate fibres

Diacetate (CA) and triacetate (CT) fibres, being esters of acetic acid, can in principle be hydrolyzed with acids and alkalis. They are resistant to dilute acids. Up to pH 9.5 alkali is said not to damage CT, CA is more sensitive. With CT an intentional alkaline hydrolysis of the fibre surface is known as an S-finish

(saponification). Alkali stains on acetate fibres are caused by cellulose arising from partially hydrolyzed acetate. They can be detected by selective dyeing with direct dyes, for example with Sirius Red 4B,[5] alternatively by Levacell Red 4B (a Bayer paper dyestuff)[148] or with 6% Benzo Black AT (Type 8000), 20% Glauber's salt, 2 min at 80 °C, liquor ratio 1:50 (different grey shades corresponding to the saponification of the acetate fibre)[149] and also by dyeing blue with zinc chloride–iodine reagent.[8]

CA is also more easily damaged by oxidizing agents than CT. The maximum ironing temperature for CA is 150 °C but it is 220–230 °C for CT. This shows that the two types of fibre also differ in their thermal resistance. Their resistance to light, ageing, microorganisms and insect attack is said to be good. Quantitative analysis of damage (damage factor) can be carried out by viscosimetric determination of the degree of polymerization. Microscopic swelling reactions with 9% caustic soda, in comparison with undamaged acetate fibres, show up chemical damage if the swelling occurs more rapidly and thermal damage when it occurs more slowly.[146]

8.5.2   Damage analysis of wool

Wool chemistry and types of damage

The chemistry of protein fibres, especially that of wool, is more complex than that of most other types of fibre. The amide groups which link the repeat units are also to be found in nylon fibres. Amides can be cleaved hydrolytically by strong acids and bases. However, the inter- and intramolecular bonds in wool are particularly numerous. There are hydrogen and disulphide bonds, salt links and hydrophobic attraction. All of these bonds are important for understanding chemical damage to wool and the possibilities for its detection.

Hydrogen bonds are already weakened by swelling in water. Urea forms a large number of hydrogen bonds and thus destabilizes the wool structure to a marked extent (see the urea/bisulphite solubility test described below). The reducing agent bisulphite attacks the disulphide bonds in cystine, another important link between protein chains. It thus also causes marked destabilization of the structure. The cystine links can also be cleaved hydrolytically, for example with hot water, steam and especially with alkali. They are relatively stable to acids. The disulphide bonds are also destroyed by strong oxidation, being converted via intermediates to cysteic acid, which can be detected by IR spectroscopy by means of the bands at 1040 and 1170 cm^{-1}.[18] In a later section it will be described in more detail how determination of the content of cystine, cysteine and cysteic acid enables conclusions to be made about damage (for example, by reduction or oxidation).

To a much larger extent than silk, wool contains many α-amino acids which either contain an additional carboxylic acid group (monoamino dicarboxylic acids such as glutamic acid and aspartic acid) or additional amino or other basic groups

(the diamino monocarboxylic acid lysine as well as arginine, tryptophan and histidine). Salt links are formed between these acid and basic side groups in the protein chain. Their maximum concentration is found in the isoionic range at about pH 4.9. Since there are more acid than basic side groups and the wool has a negative surface charge, the pH range in which wool is most stable lies slightly on the acid side (isoelectric point at about pH 4.5). The basic and acid side groups are also the reason for the high capacity of wool to bind acids and alkalis (amphoteric behaviour). Amino acids with non-polar side groups, such as leucine, proline, valine and phenylalanine, result in hydrophobic bonding and also explain the capacity of wool to absorb hydrophobic substances, for example organic solvents.

This short review is meant to illustrate the chemical bonds in wool and also to demonstrate its weaknesses. It thus becomes clear why wool is particularly sensitive to alkali, but is also damaged by strong acids, reducing agents and oxidizing agents. The effect of bifunctional wool protecting agents, such as aldehydes which cross-link amino side groups, can thus also be understood.

Indications of wool damage

First indications of possible damage to wool are a harsh handle or yellowing, both, where possible, in comparison to a wool sample before the potential damage. Heavy felting and change of shade in dyed fabrics are also signs of possible damage. Microscopic indications are usually more unequivocal, since the characteristic scale structure of wool fibres not only enables their identification and characterization but also analysis of damage to them. Changes in the scale structure can be seen particularly well in surface imprints (see Section 8.4.6). It is important here that several samples (at least 10, in critical cases up to 100) taken from different parts of the fabric are examined in order to gain a representative impression. Even in high-quality wool fabrics some individual damaged fibres can be found. Easily recognizable signs of damage under the microscope are:

- abraded scale edges or other types of scale damage (mechanical damage, kinks, rupture)
- projecting, bulky scales (for example after damage by acids, alkalis, chlorine or light)
- longitudinal striations in the interior of the fibre (damage caused by alkali or bleaching)
- pore-like openings, especially visible in embedding agents with a similar refractive index to wool (n_D 1.55, for example Canada balsam), caused, for example, by too heavy chlorination[150]
- fibrillar delamination of the wool hairs with release of the spindle cells (heavy chemical or enzymatic damage)
- frayed fibre ends (brush ends, damage by tearing, possibly indicating shoddy wool)

- root ends and skin remnants (possibly indicating slipe wool)
- crescent-shaped bites (insect attack).

Staining tests

Many dyestuffs have been described in the literature as staining tests for wool damage. Examples are:

- Methylene Blue/C.I. Basic Blue 9[7] (0.1% aqueous solution, 3 min at room temperature),
- Neocarmin W[5] and Neocarmin MS[126] (5 min at room temperature),
- Cotton Blue/Water Blue B or Telon Blue AGLF(DyStar)/Lactophenol[5, 7] (see also [Section 8.6.3](#)),
- Indigocarmin (cold saturated solution and 40 ml/l sulphuric acid),[151]
- Sirius Light Grey GG/C.I. Direct Black 77 and Sirius Light Red 4BL/C.I. Direct Red 79 (0.5% solutions, 3 min at the boil),
- Rhodamine B/C.I. Basic Violet 10[150, 125] (1% aqueous solution, 1 min at the boil),
- Congo Red/C.I. Direct Red 28 [152]

and other test dyes which are no longer commercially available (e.g. Crystal Poinceau 6R/C.I. Acid Red 28, Benzopurpurine 10B).

It is recommended that the sample be separated into the individual fibres before the staining test and that these be treated for 10 min in a solution of about 0.5% wetting agent. After staining the sample should be thoroughly rinsed.

A common factor in these staining tests is that damaged wool usually takes up more dye. Most types of damage destabilize the wool structure so that deeper dyeing takes place than in undamaged wool. Cross-linking wool protecting agents can reduce the amount of dye uptake. These staining tests should only be regarded as a rough indication of wool damage, compared with the methods described below.

The Pauly reaction as an important indication of damage

The diazo reaction according to Pauly[5, 7] is especially useful in damage analysis of wool. It shows up mechanical, chemical and biological damage and demonstrates destruction or peeling off of the cuticle (scale layer). The Pauly reaction is based on the fact that the cuticle layer contains considerably fewer aromatic amino acids than the cortex layer lying beneath it. These aromatic amino acids, especially tyrosine, react with the Pauly reagent (diazotized sulphanilic acid) to form a red monoazo dyestuff. The intensity of the coloration thus obtained, ranging from yellow-brown via orange-brown to red-brown, corresponds as a rule to the degree of damage.

The preparation of the relatively unstable diazobenzenesulphonic acid is not

very difficult,[5, 7] even in the modified form according to Doehner and Reumuth[150] as explained here: 5 g of sulphanilic acid p.a. are dissolved completely in about 2.5 ml of 10% potassium hydroxide. If necessary a few drops of potassium hydroxide are added until the solution shows a weakly alkaline reaction (pH paper). After cooling in an ice bath, 20 ml of an ice-cooled 10% sodium nitrite solution are added. This mixture is placed in a separating funnel and added dropwise to an ice-cooled solution of hydrochloric acid (8 ml concentrated hydrochloric acid and 4 ml water). After a few minutes the diazonium chloride precipitates in the form of small crystals. It is filtered off in a G2 glass filter, rinsed on the filter with a little ice-cooled water and then with alcohol. Diazobenzenesulphonic acid can also be obtained as a moist powder[153] which can be kept in the refrigerator for several months. By contrast, the light- and heat-sensitive Pauly reagent has to be prepared freshly each time. Even when cooled with ice it can only be used for a few hours.[123]

Preparation of the Pauly reagent: 0.5 g of diazobenzenesulphonic acid are dissolved in 50 ml of 10% sodium carbonate solution. After complete dissolution (careful stirring or shaking) 50 ml of distilled water cooled to 4 °C or 50 g of crushed ice are added. The solution is filled into a brown bottle and kept cooled in an ice bath during use.

To carry out the Pauly reaction the wool sample must be easily wettable. If necessary it is wetted out for 15 min in a 0.5% solution of wetting agent and rinsed carefully. The sample is then placed for 10 min in the ice-cooled diazotate solution (at a maximum of 5 °C) and then rinsed carefully with ice-cooled distilled water. A few wool fibres, still in the moist state, are then examined one at a time under the microscope, initially with intermediate magnification. Since the unavoidable decomposition products of the Pauly reagent also dye undamaged wool it is recommended to test in parallel a blank sample of undamaged wool and comparison samples with defined damage. The Pauly reaction can also be interfered with by acid and alkali residues in the wool sample, wetting agents based on fatty acids and wool protecting agents containing proteins.[150] By counting fibres under the microscope the Pauly reaction can be evaluated semi-quantitatively.[7, 150] However, Mahall[5] has reported that after very heavy alkaline damage the colour intensity of the Pauly reaction can decrease. For this reason also this test dyeing should always be combined with a microscopic examination. The Pauly reaction can also be carried out with dyed wool. However, the red coloration is difficult to see on deeply dyed wool, for example at the edges of the fibres.[5] The Pauly reaction also works with other animal hairs. In addition it shows up hair roots and skin particles, which can sometimes be present in wool yarns.

The KMV reaction for detecting acid or alkali damage

Whereas the Pauly reaction is a useful indicator of every type of damage to the cuticle layers of wool, the swelling reaction with ammoniacal potassium hydroxide according to Krais, Markert and Viertel (KMV reaction) enables the cause of

the damage to be determined, namely whether damage due to acid or alkali is present.[5, 7, 154, 155,] A further advantage of this swelling reaction is that it can also be carried out on dyed fibres. For example, fibres dyed by the Pauly reaction can be used here (after drying) so that this analysis of damage can be concentrated on the more heavily damaged fibres.

Preparation of the KMV reagent: 20 g of potassium hydroxide are dissolved in portions in 50 ml of at least 25% ammonia solution cooled in ice with occasional careful shaking or stirring. This solution is placed with a loose cover in a fume cupboard for 2 h in order for superfluous ammonia to escape. It can then be kept in the refrigerator for several months but its activity should be checked on wool samples with defined damaged before use.

Procedure for the KMV swelling reaction: the wool fibres to be tested are laid on a microscope slide, a few drops of the KMV reagent are added and the fibres observed under the microscope at intermediate magnification. The time is noted from the addition of the reagent to the appearance of the first small, hemispherical blisters on the fibre surface. The evaluation of the findings is given in Table 8.10. Irregular small protuberances slowly become larger until they finally break up. With coarse wool fibres the time taken for the appearance of the first blisters is longer than that for fine fibres. Again this illustrates that a comparison with undamaged wool and wool with defined damage is a useful aid to interpretation. In particular, the comparison of samples before and after a potentially damaging process enables a more exact explanation of the damage. When acid and alkali damage have taken place sequentially, the results of the KMV reaction are not unequivocal. Long swelling times can occur without alkaline damage if the wool has been treated with aldehydes or other cross-linking agents (as fibre protecting agents).

This qualitative analysis of acid and alkaline damage is complemented by quantitative tests as described in the sub-section below. Short swelling times in the KMV reaction are a sensitive and discriminating indication of acid damage. The longer swelling times after alkaline damage provide less discerning evidence. A further indication of alkaline damage is the particularly heavy staining with Lactophenol/Water Blue, but this is not specific, since other chemical, biological and mechanical forms of damage also cause deeper staining. Rolling up of the fibre ends to crosier forms or even more pronounced ringlet forms is, on the other hand, alone typical of alkali-damaged wool.[5]

Detection of alkali and acid residues, including formation of methyl orange crystals

A simple indication of possible damage can be obtained by measuring the pH value of the wool (liquid indicator, flat-ended pH electrode) or that of the aqueous extract, according to IWTO-2 or DIN 54275 and 54276, for example. The determination of the alkali content (IWTO-21) and acid content (IWTO-3, DIN

Table 8.10 Time until commencement of swelling of wool with KMV reagent[7,150,154]

Time until commencement of KMV reaction (min)	Conclusions about type and extent of damage
1–2	Very heavy acid damage
2–6	Acid damage
6–10	Treated with acid but scarcely damaged
10–12	Normal undamaged wool, depending on fineness and origin
15–30	Possibly treated with alkali but without noticeable damage
More than 30	Treated with alkali, in most cases also alkaline damage

54280) are standardized methods.[156] In cases where only small amounts of sample are available for damage analysis microscopic investigations with methyl orange can be useful as an alternative to these methods of direct pH measurement. A few fibres on a microscope slide are covered with a cover slip, 0.1% aqueous methyl orange solution is then added from the side. In the presence of acid, thin orange-coloured needles are rapidly formed at the fibre surface. They consist of the free acid of methyl orange, which at pH values of 4 or below is hardly soluble in water.[33, 24] This elegant method of detecting acid residues is also applicable to all other types of fibre.

Detection of damage caused by heat and light

After longer periods of exposure to heat, wool textiles can discolour above temperatures of about 120 °C. The allowable temperature for rapid pressing is about 160 to 170 °C.[157] At higher temperatures and longer periods of time wool yellows. In strong light, wool is at first bleached (photo bleaching) and then yellows (photo yellowing). This effect is intensified by additional thermal stress, for example with wool textiles in automobiles. UV absorbers lessen this damage. Alkali residues increase the extent of yellowing by heat. Further indications of this type of damage are markedly lowered peracetic acid/ammonia and urea/bisulphite solubility as well as lower cystine content. Alkali solubility and Methylene Blue uptake are increased slightly by dry heat treatments and markedly by damage caused by light and moist heat.[18] Peracetic acid/ammonia solubility enables differentiation between damage due to dry heat (markedly reduced solubility) and damage due to light (increased solubility). Additionally this is said to be a good indicator of cross-linked wool (reduced solubility). The tryptophan content can also be used as an indicator of photodegradation.[158, 159] These quantitative methods are described in more detail in following sub-sections. The increased values for solubility can be ascribed to the cleavage of cross-links, especially the disulphide bonds. The formation of new cross-links, for example the formation of lanthionine, contributes to a decrease in solubility.

Detection of biological damage to wool

Bacterial damage to animal fibres is described more often than fungal damage.[5, 147, 150] Dyed fabric damaged by bacteria, for instance, often has light spots or streaks which cannot be repaired. Typical observations on the damaged fibres are intensified striations and splitting up into cortex cells. The fact that only the orthocortex has been attacked and the paracortex remains is characteristic.[5] In order to differentiate from acid damage, in which the cortex cells can also be exposed, the KMV reaction, which is very sensitive to acid damage, is recommended. The extent of damage by bacteria can be assessed by the Pauly reaction. Bacteria can be stained with Lactophenol/Water Blue (as can fungi) and also with carbolfuchsin (1 g fuchsin, 10 ml alcohol, 5 ml liquid phenol, 100 ml distilled water; 3 min at room temperature[147]). However, the bacteria are often washed off during dyeing or scouring so that only the changes in the fibre, as mentioned above, remain as evidence. Mahall has described the procedure and the problems of detecting bacterial damage in detail.[5] The same is true for fungal damage, the microscopic detection of which is described in Section 8.6.3

Wool can also be damaged by insects. For example, the larvae of the clothes moth (*Tineola biselliella*), the furniture carpet beetle (*Anthrenus flavipes*) and the black carpet beetle (*Attagenus*) feed on keratin. Treatment with moth- and beetleproofing agents can largely prevent such damage. The damage caused by insects to non-treated wool can be easily recognized under the microscope.[120] If fibres with crescent-shaped bites are found at the edge of holes, the holes can be said to originate from the furniture carpet beetle, which sometimes also leaves behind typical hairs. According to Peter, moth larvae usually bite off the end of the fibre and leave behind typical traces of a transparent, voluminous substance, which exudes from the mouth of the larva when feeding in the vicinity of the fibre end.[24] Moth bites are sometimes also found on cellulosic and synthetic fibres, the fibre substance then being excreted without being digested. Excrement is further evidence of moth damage.

Staining tests for detecting shrinkproof treatments

The detection of shrinkproof treatments is not itself part of damage analysis but it can contribute to clarifying cases of damage. To detect chlorinated wool and Hercosett shrinkproof treatments Bayer has suggested the following staining test:

- 0.8% Supramine Yellow GW/C.I. Acid Yellow 61, replaceable by Telon Yellow GW micro (DyStar)
- 1.0% Acilan Fast Navy Blue R/C.I. Acid Blue 92, replaceable by Acid Blue 92 (Aldrich) or Sandolan Navy Blue P-RLp125 (Clariant)
- 5% sodium sulphate
- 6 ml l^{-1} acetic acid
- 2 g l^{-1} sodium acetate

- 10 min at 40 °C.

Untreated wool is dyed greenish-yellow, chlorinated wool is dyed a dirty green, Hercosett-treated wool is navy blue and wool treated with Basolan SW is dark green.

Polymer films applied to wool as shrinkproofing treatments can also be selectively stained with optical brighteners and then detected by fluorescence microscopy. The levelness of their application can also be tested in this way: the wool sample is treated with a 0.5% solution of the optical brightening agent Ciba Uvitex BHT 180% for 30 min at 0– 2 °C (cooled with ice) at a liquor ratio of about 1:100, then rinsed three times for half a minute each with cold water and dried. After UV excitation the polymer film can be recognized by its strong blue fluorescence.[49, 148]

Quantitative analysis of wool damage

The quantitative methods described here enable the degree of wool damage to be estimated and sometimes also the type of damage. The principle of solubility tests is to determine the weight loss after an exactly defined treatment and to compare this with the weight loss of undamaged wool. The weight loss is always calculated on the basis of the dry weight of the fibres and given as a percentage. As a rule, the greater the difference to the weight loss of undamaged wool the more extensive is the damage. By analogy, this also applies to the methods where the content of certain amino acids (cystine, cysteine, cysteic acid, lanthionine) or the amount of dye uptake (for example, Methylene Blue) is determined. Here also the difference from the reference value for undamaged wool is used to evaluate the damage. Table 8.11 lists the most important quantitative methods for wool damage analysis.

Solubility tests are sensitive indicators of changes to the natural surface protection layers of the wool fibre, for example, the enlargement of the porosity or penetrability after damage to the epicuticle.[160] Reagents which cause formation of new cross-links (aldehydes, chrome dyes, multifunctional reactive dyes) reduce the solubility. Since values for the solubility of undamaged wool given in the literature usually show a relatively large variation, the accuracy of the analysis is increased by comparison with a sample taken before the potentially damaging treatment. This is especially important for detecting slight damage. Sakli and Schutz[160] have described the influence of fibre fineness (increasing solubility with increasing fineness), test temperature and mechanics (shaking) on common solubility tests. Schefer[18] explained the connection between usual wool treatments in practice and the typical changes in the wool resulting from these, including possible chemical damage.

As a complement to Table 8.11 the most important simple quantitative test methods, which as a rule can be carried out in any textile laboratory, are commented on below. More complicated methods are only used for wool damage

Table 8.11 Important quantitative methods for wool damage analysis[18]

Method	Principle	Main conclusions	Value for undamaged wool	Value with very heavy damage
Alkali solubility IWTO-4 (1) ASTM D-1283 (2) BS 3568 (3) SNV 195 587 (4) DIN 54281 (5)	Treatment with 0.1 N NaOH at 65 °C, 60 min	Increase after treatment with acids or oxidizing agents, also after steaming above 100 °C	12–17%	50–80%
Urea/bisulphite solubility IWTO-11 DIN 54279	Treatment with a urea/bisulphite solution at 65 °C, 60 min	Increase after treatment with acids or oxidizing agents; marked decrease after treatment with alkali or cross-linking agents	40–50%	about 5 or 80–90%, respectively
Peracetic acid/ammonia solubility SNV 195 586	Oxidation of cystine with peracetic acid and treatment with 0.2 N ammonia	Decrease after treatment with alkali, cross-linking agents or dry heat	90–86%	60–40%
Cystine and cysteine content IWTO-15 EMPA-Methode (6)	Hydrolysis of wool with sulphuric acid, reduction of cystine with sulphite, colorimetric determination of the blue colour formed with phosphotungstic acid	Decrease in cystine content after treatment with alkali, peroxide, reducing agents (not with acids), increase in cysteine content after reduction	Cystine 11–12.5% Cysteine 0.3–0.4%	Cystine 6–8% Cysteine 1–2%
Cysteic acid IWTO-23 DIN 54286 and IR spectroscopy	Total hydrolysis, electro-phoretic separation and colorimetry or FTIR preferably with ATR	Increase after heavy oxidation, for example with peroxide or chlorine	0.2–0.5%	3–5%
Methylene Blue-uptake SNV 195 588	Staining with Methylene Blue and colorimetry of the residual liquor	Global parameter, increase with almost all types of chemical damage to wool	3–5 mmol/100 g	25–35 mmol/100 g

(1) International Wool Textile Organisation; (2) American Society for Testing and Materials; (3) British Standards Institution; (4) Schweizerische Normen-Vereinigung; (5) Deutsches Institut für Normung; (6) Eidgenössische Materialprüfanstalt

analysis in exceptional cases. They often involve the chromatographic separation of the total hydrolysate of wool samples, which is available in automated form. Schefer[161] names some exceptions to the rule that the results of quantitative wool damage analysis correlate well with mechanical textile tests, for example after cross-linking reactions.

Alkali solubility

Since alkali solubility increases particularly markedly after acid damage (from about 15% to as much as 80%) it is a sensitive indicator for this kind of damage. Damage caused by peroxide bleaching or chlorination causes a much smaller increase in solubility (usually up to about 20–30% weight loss). Alkali solubility also increases noticeably after reductive as well as oxidative damage and also after HT steam treatments. Dry heat and damage by light increase alkali solubility to a lesser extent. After damage by alkali a small decrease in alkali solubility is observed (for example, down to 10%). If the aqueous extract of the wool sample indicates a pH value below 4, the acid content of the wool should be determined and taken into consideration when calculating the solubility in the alkali solubility test as well as the urea/bisulphite solubility test.[7]

Urea/bisulphite solubility test

Since urea cleaves hydrogen bonds and bisulphite cleaves disulphide bonds, the weight loss with undamaged wool is high (40–50%). It is increased further by acid damage (up to more than 80%) and greatly reduced by alkaline damage (down to a few per cent, for example 5 to 10%), because under alkaline conditions wool forms new cross-links (lanthionine and lysinoalanine formation). Urea/bisulphite is therefore particularly useful for investigating alkali damage. Damage caused by chlorination or peroxide bleaching causes a slight increase in urea/bisulphite solubility (up to 50–60%), steaming and dry heat lead to a slight decrease.

Determination of the cystine content

Undamaged wool contains 11–12.5% of the important amino acid cystine. Alkali damage reduces this value markedly (for example, down to 8%). A smaller decrease (by about 2%) is caused by peroxide bleaching. Chlorination, acid damage, steaming and strong exposure to light also reduce the cystine content slightly. Determination of cystine content is particularly suitable for determining the extent of damage by alkali. However, it is much more complicated to carry out than the determination of urea/bisulphite solubility, which is also suitable in this case. For determination of cystine the wool sample is hydrolysed by heating with dilute sulphuric acid. The disulphide groups are then reductively cleaved by adding sodium sulphite or sodium pyrosulphite. The cysteine thus formed, together

with the cysteine originally present, give a blue coloration on addition of phospho-tungstic acid (Folin's reagent). The colour is then assessed colorimetrically. This method of determining cystine content can be interfered with by some dyestuffs on dyed wool. Interference can also occur after oxidative or reductive treatments.[7]

Determination of the cysteine content

The cysteine content is determined analogously to the cystine content but without addition of reducing agent. The cysteine content has to be taken into consideration when calculating the cystine content, even though undamaged wool only contains 0.3–0.4% cysteine. This value is increased markedly by reductive treatments (bleaching, anti-chlorine treatments, stripping of azo dyes), which can thus be checked by this method. The cysteine content is lowered by alkaline scouring, setting and decatizing processes and oxidative treatments such as peroxide bleaching. Complexing agents based on ethylenediamine tetra acetic acid can interfere with the determination of cysteine.[162] Damage caused by reductive treatments should be readily assessable by determining cysteine content. However, according to Schönberger, increased cysteine values are seldom found in investigations of complaints.[163]

Determination of the tryptophan content

Tryptophan can be used as an indicator amino acid for the photolysis of protein fibres, such as wool, silk or human hair. Schäfer[158] has compared different methods for the quantification of tryptophan and the interference to the colorimetric method (with dimethylaminobenzaldehyde) caused by pigments and dyes.

Cumulative wool damage

Damage to wool is often due to a combination of several causes, whereby according to Doehner and Reumuth[150] the effects can be developed, added, multiplied or even increase exponentially. When more than one chemical acts on wool, as is usually the case in dyeing and finishing, damage can occur which would have been harmless if each of these chemicals had acted alone. This effect is known as cumulative damage. For example, intensive peroxide bleaching and dyeing in strong acid conditions can each be carried out alone in such a way that the performance of the wool is not lessened and other undesirable effects are also avoided. If, however, these treatments are carried out under the same conditions in sequence, the wool suffers considerable damage. Sanger[164] explained this by the catalytic effect of the cysteic acid formed during oxidation on the acid hydrolysis of the neighbouring amide group. The proton from the cysteic acid is transferred via a hydrogen-bond-stabilized six-membered ring structure to the amide nitrogen, which makes this amide group easier to hydrolyze.

In this section on wool damage analysis we have hoped to show that the fascinating, multifaceted chemistry and structure of wool give rise to many possibilities for wool damage but also to many methods of chemical analysis.

8.5.3   Damage analysis of silk

Reports on faults with silk fabrics are more common than would be expected from their share of the world fibre market (about 0.1%). One reason for this is that silk is particularly delicate. Mechanical treatment, especially in the wet state (dyeing and finishing as well as household laundering), causes irreparably abraded areas, the so-called blanched places. Defibrillation and splitting off of the silk filaments causes incident light to be scattered diffusely. The silk lustre is no longer present, the fabric appears dull and lighter. This is particularly noticeable with dark dyeings. The abraded fibres can be identified in direct microscopy and even better in surface imprints. The same is true for silk lousiness (exfoliation), which is not actually a case of damage but does represent a quality problem. Silk lousiness is the term for pills formed from fine fibrils which become separated from the filaments of the silk. They are laid bare during degumming and during further processing they are twisted together into pills.[165] Again they represent an aesthetical problem especially for dyed fabrics.

A further common type of damage in silk is alkali damage, which usually occurs during degumming, especially when fibre protective agents are not used. Typical mechanical and chemical damage during scouring has been described in the literature.[166] According to Kornreich[167] chemically damaged silk dissolves in cupriethylenediamine, whereas undamaged silk does not dissolve. Damage to silk by alkali was evaluated by determination of the content of amino groups by the ninhydrin method and by determination of the tensile strength.[168] Silk should not be washed with products that contain hypochlorite or proteases, which are recommended for cellulose textiles. Further typical forms of damage to silk and their analysis have been described by several authors.[169–174]

Mahall and Goebel have reported that the Pauly reagent as used in wool damage analysis can also detect mechanical and chemical damage to silk, although the silk fibre does not have a cuticle layer but only a thin fibroin sheath.[5,] [165] With silk the Pauly reaction thus has to be carried out for a short time and with cooling (1–2 min, ice-cooled). To help verify the results it is recommended that comparisons be carried out on undamaged silk and on silk with defined damage. In addition, before this analysis is made Bombyx mori silk has to be carefully checked to see if it is completely degummed, since residues of sericin are stained red in a similar way to damaged fibroin. Undamaged Bombyx mori silk is stained yellow. Degummed tussah silk is stained yellow-brown by the Pauly reagent and bleached tussah silk light orange, thereby indicating a slight degree of bleaching damage.

Similar staining tests have been described for the detection of sericin and for

controlling the degumming process: staining of silk with a 2% aqueous solution of C.I. Direct Red 80 at a liquor ratio of 1:40 for 2 min at the boil[175] or with 1 g l^{-1} C.I. Direct Red 80 at a liquor ratio of 1:200, also for 2 min at the boil.[176] C.I. Direct Red 80 is now available as Sirius Red F3B (DyStar), Ciba Solophenyl Red 3BL 140%, and Direct Red 80 (Aldrich). Former trade names mentioned in the literature are Sirius Red F3B 200%, Solar Brilliant Red BA 150% and Solophenyl Red 3BL 140%. Mahall and Goebel[165] have described a staining test with a 1 % solution of C.I. Direct Red 80 for 1 min at room temperature. In all these staining tests the fibroin is colourless after rinsing and the sericin is stained red. According to the manufacturer's information[126] Neocarmin W stains fibroin gold-yellow and sericin blue to violet, according to Mahall, Neocarmin W also stains degummed Bombyx mori silk blue, brownish violet or reddish violet, depending on its origin, but the colour is lighter than that with sericin.[5] Checking the stained samples under the microscope is in all cases useful in verifying the findings. Testing of degumming can also be made, in a time-consuming way, by quantitative determination of the primary amino groups after staining with ninhydrin.[176]

In order to distinguish cultivated Bombyx mori silk from wild silks such as tussah the so-called silk reagent is used. In contrast to tussah silk, Bombyx mori silk dissolves completely after 2–5 min at room temperature.[29] Preparation of the silk reagent: 10 g of copper sulphate are dissolved in 100 ml of distilled water and 5 g of glycerine added. 40% sodium hydroxide is added dropwise until the copper hydroxide precipitate initially formed is completely dissolved. Two further reactions for differentiation have been described by Agster.[7] Bombyx mori silk dissolves in boiling zinc chloride solution (45° Bé) after 1 min, whereas tussah silk is hardly affected. Unlike tussah silk, Bombyx mori silk is also dissolved after boiling for 5 min in 5% sodium hydroxide. Mahall[5] has illustrated the microscopic differentiation between cultivated and wild silk by means of longitudinal views and cross-sections.

Since weighted silk is more easily damaged mechanically and the detection of weighting is an important aspect of quality control, this subject will be mentioned briefly. Weighting with minerals, usually with tin-phosphate-silicate, results in a light-coloured skeleton residue of ash after burning. At higher levels of weighting the structure of the yarn or fabric is retained in the ash. Agster[7] has described conventional chemical detection reactions for weighting. Silk can also be weighted by grafting-polymerization with methacrylamide,[177] which can be detected by conventional chemical analysis or by IR spectroscopy.[178]

8.5.4   General types of damage to synthetics (thermal, light and mechanical damage)

In contrast to natural fibres only a few simple test methods are known for damage analysis of synthetic fibres. On the other hand the standard synthetic fibres are also generally much less heavily damaged by acids, alkalis and microorganisms than

are cellulosic and protein fibres. But there are also typical faults and types of damage to synthetic fibres, as is briefly described in this section.

Thermal damage

Thermal damage is one of the most frequent causes of complaints about synthetic fibres, especially if they have a relatively low melting point. It causes, amongst other things, hardening of handle, yellowing, loss of strength, uneven fabric appearance (light reflection) and dyeing behaviour (spots, streaks and other types of unlevelness such as warp splashes). Thermal damage can occur at many stages in processing. Examples are texturizing, setting, singeing, pressing and sewing. During texturizing the originally circular fibre cross-sections are usually flattened to polygons. When setting is at too high a temperature or for too long, the yarns are flattened at the interlacing points. During singeing of staple fibre blends with cellulosics or wool, protruding synthetic fibres can melt to form small balls, which cause a hard handle and which dye more deeply in exhaust processes (small dark spots, deeper dyeing being caused by the high amorphous content and the decrease in relative surface area) and after continuous dyeing are lighter than the undamaged fibres (the diffusion time is too short for the melt balls).[5] Pressing at too high a temperature causes flattening and bonding of thermally sensitive synthetic fibres. Thermal damage also occurs through friction, impact, striking, cutting or punching out during textile production and garment manufacture. Mahall has shown many typical examples of this.[5] The most important methods of investigation of thermal damage are microscopy in longitudinal view (also with surface imprints) and on cross-sections, dyeing tests and thermal analysis (see Section 8.4.5). Schwertassek[179] has compared methods for determining the degree of setting in synthetic fibres, since differences in setting are a common cause of unlevel dyeing:

- The critical solubility temperature, which also depends strongly on fineness, crimp, delustrant and residues of auxiliaries. In addition, relatively long sections of yarn are necessary.
- Iodine sorption, which can be used for many types of fibre. Residues of some chemicals interfere. Also, only fibres of the same fineness can be compared, since the adsorption is strongly dependent on the specific surface area.

Buchanan and Hardegree described the influence of heat and tension (for example during drawing, texturizing and occasionally dyeing) on faults in yarns made of polyester, nylon 6,6 and polypropylene.[180]

Damage by light

According to their chemical constitution and stabilization synthetic fibres show differing degrees of sensitivity to light, for example aliphatic and aromatic polyamides are more sensitive and polyacrylonitrile fibres less so. Apart from

some technical fibres, synthetic fibres are usually delustred with titanium dioxide. This catalyses photolytic degradation (photolysis), which can be recognized by an apparent coarsening of the grains of the delustrant. The delustrant pigments appear larger because they are surrounded by a sphere of degraded fibre substance with a different refractive index.[33, 34] Damage by light can usually be detected by fibre-specific reactions and also by non-specific effects such as yellowing, loss of strength and decrease in the average degree of polymerization.

Mechanical damage

Mechanical damage to synthetic fibres can be just as easily detected under the microscope as with natural fibres. In the case of thermoplastic fibres mechanical damage is often accompanied by thermal damage. This causes deformations which can be clearly seen in the longitudinal view and in fibre cross-sections. The change in reflection of light in the damaged area interferes with the uniform appearance of the fabric. Well-known examples are shuttle marks and warp splashes, caused by the shuttle striking yarns in the shed of the loom and thus deforming warp or weft threads made from synthetic fibres. The higher lustre of the deformed threads then shows up at a certain distance from the selvedge in the form of short, irregular and diffuse streaks in weft direction.[5] Hearle studied the structure of ruptured fibres (polyester, nylon, acrylic) under the light microscope and with electron microscopy and also the damage caused by abrasion and torsional stress, the samples mainly coming from damage in use.[181]

Differences in drawing ratio, fineness or texturizing of synthetic fibres are often the reason for streaks and barriness in fabrics made from them. They can be identified by marking the threads, stripping off the dye and redyeing, in which case they reappear at the marked places. These faults can usually be recognized under the microscope (surface imprints) and differences in drawing ratio can be seen particularly well in polarized light.[182] A milky dullness in synthetic fibres can be caused by tiny gas bubbles formed either during coagulation in the precipitating bath or by thermal degradation during finishing. They can be easily recognized under the microscope.[21] Irregular distribution of the fibre components in yarns made from staple fibre blends, usually from synthetics with natural fibres, can lead to a skittery fabric appearance. This can be checked by microscopy of the yarn cross-section.[23]

Chemical damage

The chemical weak spots and the corresponding types of damage vary greatly with synthetic fibres depending on their structure. Thus they are described in the next section in relation to the type of fibre. However, a general difference in chemical stability exists between fibres formed by polymerization or polycondensation. At extreme pH values polycondensate fibres are hydrolytically degraded, for example

by cleavage of ester or amide bonds between the constitutive elements. The carbon backbone chain of the polymerisate fibres is stable to hydrolysis but sensitive side groups such as the nitrile groups of acrylic fibres can be hydrolyzed.

Microfibres

Microfibres are especially sensitive to light damage, owing to their large specific surface. Light damage is intensified by the catalytic effect of some dyes and their light degradation products. Also a much higher dyestuff concentration is needed for microfibres, compared to the same shade on normal fibres. Fastness problems can arise from residual size that is usually not completely washed off from the microfibres.

8.5.5   Analysis of damage to polyester fibres

Polyester fibres (PET) are chemically relatively stable, so that damage caused by acid or alkali is seldom. At extreme pH values, however, hydrolytic degradation occurs, for example as used in the alkaline titre reduction of polyester textiles. Thermal damage is more common, caused by setting, pressing, pleating or singeing fibre blends containing PET or thermally bonding nonwovens at too high temperatures. Another form of thermal damage is the thermal deformation caused by heat of friction, which can occur during sewing and cutting or punching out. Mahall has described many examples of this.[5] The damage caused by excessive heat and mechanical effects, for example during primary spinning,[183] secondary spinning[184] or tension during setting, primarily causes structural differences in the PET fibres which lead to barry dyeings and shade differences across the fabric. Differences in shade can be detected with as little as 2 °C difference in setting temperature, depending on the sensitivity of the disperse dye used. Generally speaking, at setting temperatures above 185 °C markedly deeper dyeings are obtained.

As a test dyeing to detect structural differences in PET, C.I. Disperse Blue 79 (for example Dianix Navy Blue NNG, Foron Navy S-2GL or Ostacet Navy Blue 2 GLS) has been recommended, for example for 30 min at 130 °C.[185] Another test dyeing uses a mixture of a blue dye which shows up structural differences very markedly and a yellow dye which does not have this property:[186]

- 0.3% C.I. Disperse Blue 130, for example Ciba Terasil Navy BGLN 200%
- 0.15% C.I. Disperse Yellow 122, for example Ciba Terasil Yellow 2GL
- 1 gl^{-1} ammonium sulphate
- 0.5 gl^{-1} Uvadin DP
- pH 5, set with formic acid, liquor ratio 1:20

Heat at a rate of 5 °/min to 50 °C, then at 1.5 °/min to 90 °C and at 0.5 °/min to 130 °C. Treat at 130 °C for 30 min and cool at 3 °/min to 60 °C (or dye at the boil for 60 min with 1 g l^{-1} carrier)

Table 8.12 Validity of test methods for changes in structure of PET due to heat and tension[187]

Test method	Effect of heat	Effect of tension	Equipment costs	Effort
Dye uptake during HT dyeing *	–	–	Large	Large
Residual shrinkage ** (hot air)	+	++	Low	Low
Tensile strength	–	–	Large	Low
Elongation at break	–	+	Large	Low
Work at 5–10% elongation	–	++	Large	Low
Elongation at 200–300 cN	–	++	Low	Low
Residual extension	–	++	Low	Low
Critical solution time * (phenol)	–	–	Low	Large
Density (graduated column[188])	++	–	Medium	Medium
Differential scanning calorimetry (DSC)	++	–	Large	Low
Thermomechanical analysis ** (TMA)	+	++	Large	Low
X-ray (long period)	+	–	Large	Large

Effects of heat and tension: * simultaneously, ** separately.
Validity: – none, + good, ++ very good.

Rinse hot and cold and reductively clear with:

- 5 ml l⁻¹ sodium hydroxide 36 ° Bé
- 2 g l⁻¹ hydrosulphite
- 1 g l⁻¹ Eriopon OL

for 20 min at 70 °C, then rinse, neutralize and dry.

Differences in draw ratio in PET fibres can be analysed by microscopic determination of their specific birefringence, whereby higher tension results in a higher birefringence whereas the influence of temperature varies.[39] In Section 8.4.5 it was described how the thermal prehistory of PET can be analyzed with the aid of the so-called effective temperature or middle endotherm peak temperature (MEPT) determined by differential scanning calorimetry. The term 'effective temperature' was introduced by Berndt and Heidemann.[187] In this publication a review of many other testing methods for analysing structural differences in PET is given, including an evaluation of how well they respond to the influence of heat and tension. Table 8.12[187] shows that the methods of thermal analysis are fairly well suited to this purpose. Investigation of the fine structure of PET with the aid of iodine sorption has been described by Gacén and coworkers.[189,190]

According to Richter[191] damage caused by alkali can be recognized from the partial saponification number and damage by heat from the iodine sorption. Bobeth[192] analysed thermal damage and damage caused by dyeing and finishing on the basis of swelling of cut ends and microsolubility times. Schwertassek[193] determined differences in degree of setting by various methods. According to Küppers[194] the influence of strong heat and in particular of setting conditions can be seen under the microscope in a 90% phenol solution (Table 8.13). Since the

Table 8.13 Setting conditions and swelling time of PET fibres in 90% phenol solution[194]

Commencement of longitudinal swelling after (min)	Exposure to heat, setting conditions
15 to 30	Untreated or slightly set
About 60	Normal setting
More than 120	Overset, thermally damaged

swelling time is dependent on the origin of the polyester fibres, comparisons should only be made between fibres from the same batch, for example from samples before and after thermal damage. In addition, the samples should not be heated during the swelling test, for example by leaving them for a longer period of time on a heated microscope stage (this results in shorter swelling times). The older methods for investigation of damage to PET fibres mentioned in this paragraph are seldom mentioned in the recent literature. More common is the determination of the average degree of polymerization of damaged polyester by means of viscosimetry in *m*-cresol.[195] According to Tetzlaff and co-workers normal DP values range from 80 to 150.[196]

A simple staining test which indicates mechanical, thermal and chemical damage to polyester fibres consists of staining with an oil dye dissolved in *m*-cresol, which according to Stratmann[8] is also used to identify different polyester fibres (a more advantageous alternative with alcoholic potassium hydroxide is discussed in Section 8.4.1).

Preparation of the test staining solution: 0.5 g of C.I. Solvent Red 27, for example Oil Red O (Aldrich, Fluka, Sigma), in the literature recommended as Oil Red 5B, is wetted with a little methanol and then dissolved in 50 ml *m*-cresol.

Carrying out the test: to identify the fibre short snippets of fibres are squeezed off with blunt scissors. To analyse the damage the fibre is treated as gently as possible and, if necessary, cut with a sharp instrument. The fibre sample is treated for 5 min at room temperature with the solution of oil dye. It is then rinsed thoroughly with methanol, very briefly with acetone and immediately thereafter again with methanol. The squashed areas of the polyester fibres are dyed intensively, fibres damaged mechanically, chemically or thermally are dyed deeply in the damaged area whereas undamaged Kodel fibres are dyed overall.

Using a staining test with C.I. Basic Blue 3 (Astrazon Blue BG) PET fibres which have undergone titre reduction by alkali treatment can be identified,[197] whereas by spraying with Astrazon Pink FG (0.5% in dichloromethane) they can be tested for barry dyeing.[198]

Photolytically damaged polyester fibres can be recognized under the microscope by the apparent coarsening of delustrant grains,[199] as described in Section 8.5.4, and by fluorescence in UV light of the degradation products oxy- and 2,5-dihydroxy terephthalic acid.[200, 201] This fluorescence microscopy enables a

differentiation to be made between photo and thermal damage, but only if optical brighteners do not superimpose on the weak fluorescence of the terephthalic acid derivatives.

Since they are hydrophobic, PET fibres show great affinity for other hydrophobic substances, not only to disperse dyes but also for oils, grease and waxes as used in textile production. If these contaminants are not removed during pretreatment and they can diffuse into the PET fibres during thermal treatments (such as setting, thermosol dyeing or pressing) they are often well fixated and are thus a typical cause of stains, streaks and other similar types of complaint. They can be detected by extraction followed by TCL or IRS as well as under the microscope by staining with oil dyes and also by dulling the film in surface imprints (see Section 8.6.1).

Polyester oligomers as a cause of damage

PET oligomers are low molecular weight side products of the polycondensation reaction with two to about 10 repeat units. These linear and cyclic oligoesters are possibly also formed during the melt spinning process. The total content of oligomers is 1–3% and 70 to 90% of this amount is in the form of the cyclic trimer *cyclo*-tris-ethylene glycol terephthalic acid ester, $c(G–T)_3$. A large percentage of the cyclic trimer diffuses onto the fibre surface under HT dyeing conditions and from there into the dyebath. $c(G–T)_3$ is practically insoluble in water up to 100 °C and at 100–140 °C only to the extent of 1–5 mg l^{-1}. Thus during dyeing and in particular during cooling down of the dyebath it can precipitate and deposit on the goods being dyed or on the interior surfaces of the dyeing vessel. The problems which thus arise are particularly great when dyeing loose fibres or yarns. These problems include dust formation, poor running properties, difficult spinnability and increased wear on thread guides and needles. With piece dyeings the oligomer deposits can cause light spots, especially due to a filtration effect on the HT beam dyeing machine (possible perforation imprints on the fabric roll),[44] but less so with knitted goods in jet dyeing machines. In addition, the fabric then lacks brilliance; a cloudy greyness gives an uneven fabric appearance. Oligomers which adhere to the fibre surface particularly interfere (surface oligomers, as opposed to core oligomers). They are often mixed with spinning oils and other auxiliaries or with dyes and can be difficult to remove. In spite of many known methods of avoiding oligomer problems, such as pretreatment in an alkaline medium or with organic solvents, alkaline dyeing, addition of auxiliaries, dropping the dye liquor under HT conditions and alkaline reductive clearing, PET oligomers still repeatedly cause complaints.

The first indication of damage caused by PET oligomers is often the appearance of the fault: light grey deposits, which are partially easy to remove mechanically and form dust. In addition, when an isolated sample is shaken in isopropanol a marble-like suspension with mother-of-pearl lustre is formed.[202] Detection methods

for PET oligomers, especially for $c(G–T)_3$ have in some cases already been described:

- IR spectra resemble that of the PET fibre (see Section 8.4.4);
- TLC detection, especially by comparing with authentic samples (see Section 8.4.3);
- melting range 305–327 °C, according to their purity (marked difference to PET fibre dust, which melts at 250–255 °C), possible confirmation by means of mixed melting points: a mixture of approximately equal parts of sample and authentic cyclotrimer should not show any marked depression of the melting point;
- microscopic detection by recrystallization on the microscope slide: dissolve in dichloromethane, $c(G–T)_3$ crystallizes out after concentration by evaporation of the solvent[202] or formation of crystals after melting the sample on the microscope slide.[5] The crystals thus formed are usually hexagonal, sometimes also in the form of needles or are star-shaped and they appear golden yellow to multicoloured in polarized light.[202]

Quantitative determination is usually made gravimetrically, after extraction with dichloromethane or dioxane, whereby a separate extraction with petroleum ether is made to determine the quantity of extractable spinning oils. In this way the maximum fraction of extractable oligomers is determined, not the total oligomer content.[202] The marked UV absorption at 250 nm also enables quantitative determination. More details of quantitative analysis can be found in the literature[7, 202] and further information, also on repairing faulty pieces, is available.[202]

8.5.6   Analysis of damage to nylon fibres

In terms of quantity standard nylon fibres were overtaken by polyester fibres around 1975. The reason that the latter fibres are now by far the most important group of synthetic fibres has also to do with the fact that nylon 6 and 6,6 fibres are more sensitive to light and less stable to hydrolysis than polyester fibres. Nylon fibres also have a greater tendency to yellowing in heat, nylon 6 in particular being less stable to heat than PET (see Table 8.6). On the other hand the abrasion resistance and bending strength of nylon fibres is very high. Hearle has described the microscopic analysis of fatigue appearance in nylon fibres.[181] Under extreme conditions of use and also during dyeing and finishing oxidative damage can occur, often intensified by heat and/or light. UV radiation damages aliphatic polyamides and the aramids. With nylon 6 and 6,6, acid damage and, less commonly, alkaline damage are usually the result of inappropriate dyeing and finishing treatments. At extreme pH values their amide bonds are cleaved hydrolytically. Comparison of the sensitivity to damage of the standard nylon fibres shows that nylon 6 is more sensitive to hydrolysis and heat whereas nylon 6,6 is more easily damaged by oxidation.

Table 8.14 Extent of damage and staining of acid-damaged nylon fibres with Rhodamine B[203]

Extent of acid damage	Staining	Loss of strength (%)
No damage	Colourless	0
Slight damage	Pale pink	about 5
Medium damage	Pink	about 15
Heavy damage	Red	about 30
Very heavy damage	Deep red	about 70

Detection of acid damage

According to Bubser and Modlich[203] acid damage to nylon fibres can be detected in a simple way by a staining test with Rhodamine B (C.I. Basic Violet 10, available from Aldrich, Fluka, Sigma): the sample is placed for 5 min at room temperature in an aqueous solution of 0.1% Rhodamine B, to which 10 ml l^{-1} of 60% acetic acid have been added. The sample is then rinsed cold until the rinsing water is colourless. Depending on the degree of acid damage, staining of the sample ranges from colourless via pale pink with slight damage to dark red with heavy damage (Table 8.14). Nylon fibres damaged by heat, light or oxidation are not stained in this test.

According to the literature[21] (see section S087 there) damage due to mineral acids can easily be recognized under the microscope by means of the irreversible swelling of the nylon fibres. Acid residues can also be detected microscopically by embedding the sample in 0.1% Methyl Orange solution (typical needle formation, see Section 8.5.2).

Detection of thermal damage

When treatments such as setting, pressing, pleating or singeing of nylon fibres are carried out at too high temperatures, and also during thermal bonding of nonwovens or during cutting and sewing, fibre deformation, fibre bonding and formation of melt balls at the fibre ends can occur, all of which can be easily recognized under the microscope. The melt balls usually dye more deeply[148] and give rise to a hard handle. Damage caused by setting can be roughly estimated by measuring the swelling time in sulphuric acid.[179, 204] Differences in degree of setting can be determined by means of a test dyeing in a 1% solution of C.I. Direct Blue 71, for example Sirius Blue S-BRR from DyStar (pH 5 set with acetic acid, liquor ratio 1:50, 60 min at the boil): with increasing degree of setting the dye uptake at first decreases; with overset fabric, however, it increases. The same test dyeing (or also with just 0.25% dye and an additional 1% salt) is also used to identify structural differences that have other causes which also affect dye uptake capacity, for example differences in draw ratio or texturizing. Setting differences in carpet yarns

giving streaky dyeings can be rapidly detected by spectroscopy in the near-infrared region.[205] Damage from the effect of dry heat for longer times can lead to a reduction in the concentration of amino end groups so that the staining test with ninhydrin gives a lighter colour.[206]

Detection of damage by light

Despite photostabilization during fibre production and, in some cases, additionally during finishing, damage by light (especially UV light) is fairly common with nylon fibres. The complex photolysis reactions are accelerated by delustrants as well as by contaminants within and external to the fibre (and, among many other things, by nitrous gases).[206–208] These reactions cause yellowing and loss of strength and can be recognized under the microscope by the apparent coarsening of the delustrant grains (see Section 8.5.4). According to Bubser and Modlich[203] damage by light can also be recognized microscopically by a dark dulling of the nylon fibres when embedded in olive oil. The reduction in content of amino end groups as a result of damage by light is the basis for two dyeing tests: a lighter dyeing with C.I. Direct Blue 67 (Aldrich, former Solar Brilliant Blue A 330%) (0.1% solution, 2% fatty amine ethoxylate as a levelling agent, for example Sandogen NH liquid, pH 6, 60 min at the boil)[75] and a lighter coloration with ninhydrin (0.5% solution, 2 min at the boil, short rinse and dry between filter papers). This is in contrast to damage by acid or oxidation, which gives a deeper colour in the ninhydrin reaction.[194, 206] In exceptional cases, if the effort can be justified, determination of the amino end groups with 1-fluoro-2,4-dinitrobenzene (FDNB method) gives a more exact analysis of the damage than is possible with ninhydrin. This method is also suitable for aramid and polyimide fibres.[209]

Detection of damage by oxidation

With the ninhydrin staining reaction mentioned above a darker colour than normal is obtained after oxidative damage.[194] Using modified zinc chloride solutions (Frotté reagent I and II) nylon fibres can be distinguished and identified by the so-called Frotté reaction according to Koch[31] (crenellated, finely structured transverse folds and cracks on the fibre surface, which gradually change to coarser structures and then dissolve, see Table 8.1). With solutions of zinc chloride, potassium iodide and iodine (zinc chloride–iodine reagent: 66 g $ZnCl_2$ and 6 g KI in 34 ml water, plus as much iodine as will just dissolve), modified according to Bubser and Modlich (three parts by volume of zinc chloride–iodine reagent, one part by volume of 96% ethanol, 1 part by volume of distilled water), the Frotté reaction only occurs after oxidative damage, but not after damage by acid, heat or light.[203]

This is described in more detail in Table 8.15 and is shown in Table 8.16 in a review together with other methods for detecting damage to nylon fibres. The conclusions which can be drawn from these microscopic methods are unfortunately

Table 8.15 Damage to nylon fibres and Frotté reaction with modified zinc chloride–iodine reagent, according to Bubser and Modlich[203]

Type of damage	Loss of strength (%)	Swelling behaviour after 3 min at room temperature
None (grey fabric)	0	Marked Frotté reaction
Slight acid damage	about 5	Marked Frotté reaction
Medium acid damage	about 15	Moderate Frotté reaction
Heavy acid damage	about 35	Marked flattening of the crenellations
Very heavy acid damage	about 70	No Frotté reaction
Heat set	about 15	Marked Frotté reaction
Overset	about 30	Marked flattening of the crenellations
Thermal damage	about 60	No Frotté reaction
Damage by light	about 40	No Frotté reaction, dulling of the unswollen part
Oxidative damage	about 80	Marked Frotté reaction

Table 8.16 Review of detection methods for damage to nylon fibres[148, 194, 203]

Damage due to:	Acid	Heat	Light	Oxidation
Rhodamine B staining	+	–	–	–
Swelling in modified zinc chloride–iodine reagent	–	–	–	+
Ninhydrin colour reaction	Darker	Lighter	Lighter	Darker than normal
Embedding in olive oil		Normal	Dull	
Staining with acid dye				Darker than normal

often not exact enough and can only serve as a rough guide,[123] probably also because in practice different types of damage are superimposed, for example, light and heat or light and oxidation (photo-oxidation) or even all three causes of damage together.

Viscosimetric determination of the average degree of polymerization (DP), usually in *m*-cresol,[210] enables the extent of many types of damage to nylon fibres to be determined exactly, since most types of damage occur with chain degradation. But the type of damage itself cannot be analysed in this way. In addition, contaminants which deposit on the fibre during production, dyeing and finishing or in use, and which are sometimes difficult to remove, interfere with the determination of DP. According to Zaremba *et al.* usual DP values for PA6 range from 100 to 180 and for PA6.6 from 50 to 80.[211]

Nylon oligomers

In the production of nylon fibres, especially nylon 6, oligomers can also be formed. They are soluble in water, as is also the monomer caprolactam, and thus they do not

usually lead to problems as do the polyester oligomers. An exception to this has been described by Schwertassek.[212] Insufficient removal of caprolactam and nylon 6 oligomers can lead to marked fibre deformation and cracks during heat setting. These deformations can be seen by embedding microscope samples in iodine/ Glauber's salt solution (40 g of potassium iodide and 5 g of iodine in 50 ml of distilled water, then diluted 1:5 with Glauber's salt solution saturated at room temperature), which also serves to identify the cause of the damage. Caprolactam and oligomers take up more iodine and can be readily seen under the microscope as yellowish brown droplets (Glauber's salt hinders their dissolution).

8.5.7   Analysis of damage to acrylic fibres

Acrylic fibres (PAN) for the home furnishings and garment sector are one of the fibre types with the greatest range of variation in their commercial types, similar to the elastane fibres. Two possibilities of variation in the manufacture of acrylic fibres are characteristics of this: first, the type and amount of comonomers added to make the structure more flexible and to enable dyeing with basic dyes and secondly the possibility for wet or dry spinning with different solvents. Additional special features are dope dyeing and gel dyeing. The resulting variety of types is a cause of many cases of damage caused by mistaken types and dyeing faults. PAN fibres have good resistance to acid up to medium concentrations and somewhat poorer resistance to alkalis. Their biological resistance is good. PAN fibres are very resistant to non-polar organic solvents, oxidizing agents and weathering. Their abrasion resistance is low because of a tendency to fibrillation.[213] Resistance to heat is also relatively low; above 150 °C they show yellowing and, depending on the type of fibre, from 200–250 °C an exothermic cyclization takes place (discoloration from yellow to brown and then black, caused by naphthyridine structures). This short review shows that with PAN fibres one can expect damage from heat, abrasion, polar solvents and effects of strong alkalis to be predominant. In addition, damage is also caused by too great or uneven shrinkage, the reason for which can be found in fibre manufacture, textile production or dyeing and finishing.

Mechanical damage

Mechanical damage is usually easy to recognize under the microscope, especially in surface film imprints. Hearle has analysed abrasion and torsional damage with light and electron microscopy.[181] Microscopic swelling and solubility tests have been developed for analysing mechanical and, in particular, thermal damage. The microsolubility time in 56% nitric acid decreases after mechanical damage to an extent which depends on the form of the fibre cross-section.[192] Abraded spots, fibrillated and squashed fibres and thermomechanical damage appear lighter in dyed fabrics because of the greater scattering of light.[5]

Thermal damage

The influence of cold or hot stretching in combination with heat setting has been investigated by many physical and chemical methods, which are also suitable for corresponding damage analysis (amongst others porosity, density, strength, extensibility, differential thermal analysis, molecular weight, electron microscopy).[214] The iodine adsorption number according to Schwertassek (mg iodine taken up by 1 g fibre) is very dependent on the PAN fibre type and is reduced by the effect of heat.[191] With the same fibre material, differences in solubility in dimethylformamide demonstrate differences in thermal effects (lower solubility after more drastic thermal effects).[194] With some types of PAN fibre so-called vacuoles are formed at temperatures around 90 °C. These are hollow spaces which have an effect like delustrants and feign apparent unlevelness of dyeing. They are particularly visible under the microscope when the sample is embedded in benzene/chlorobenzene 1:1.[194] Schmidt[34] reported a case of damage in which a deepening of the colour occurred during steaming for form setting. This was due to a reduction in the number of vacuoles during steaming.[34] A large amount of acrylic fibre production is used to produce high-bulk yarn. This is made from a blend of acrylic fibres with different morphology (fully shrunk fibres and shrinkable fibres, where the shrinkage is produced by heat treatment after spinning the yarn, the bulk effect then arises from the loops formed by the preshrunk fibres). By measuring the critical solubility time in common solvents (dimethylformamide, dimethylsulphoxide, dimethylacetamide) Gacén and Arias[215] developed a simple test which shows differences in fibre structure and shrinkage behaviour sensitively and accurately (the less the fibres have been shrunk the shorter the solubility time). This method was also used for development and endurance testing of technical textiles, including those made of PAN fibres.[216]

Damage by acids and alkalis

Since the main polymer chain of PAN fibres consists of carbon atoms, it is stable to hydrolysis. The nitrile side groups and many of the comonomers used to make the structure more flexible, such as methyl acrylate, methyl methacrylate or vinyl acetate, are cleaved at extreme pH values. The ester groups are hydrolysed to the original acids and alcohols and the nitrile groups are saponified to the acrylic acid structure via the amide intermediate. The loss of nitrogen or ammonia which thus occurs forms the basis of an analysis of alkali damage to PAN fibres, namely the determination of the partial nitrogen number according to Richter.[191] This also decreases owing to the effects of dry and wet heat, whereby the latter (steam) causes more damage (cleavage of the strong intermolecular hydrogen bonds in PAN). Richter also investigated the copper binding capacity of PAN fibres, which decreases after steam treatment (cupro numbers I and II). Polyacrylonitrile modified with vinyl chloride (modacrylic fibres) is especially sensitive to alkali; it can be damaged by hot alkaline scouring.

Further types of damage, reasons for faults and detection methods

The widely varying dyeing behaviour of the different types of PAN fibres is a common cause of faults, for example by mistaking the type of fibre or using unsuitable dyeing methods. PAN fibre types can be distinguished microscopically by their different swelling and fibrillation in zinc chloride–iodine reagent. Simple staining tests have been published for testing differences in dye uptake capacity (1% C.I. Basic Blue 5, Aldrich, formerly Astrazon Blue B, 1.5% sodium acetate, 1.5% acetic acid 60%, 1% Avolan IW[194] or 1% C. I. Basic Blue 3, for example Astrazon Blue BG micro 200% or Maxilon Blue 5G, set to pH 4.5 with acetic acid[217]). Heinkel has also described dyeing tests to distinguish PAN fibres with sulphonic and carboxylic groups (2% Maxilon Black T, pH 2 set with sulphuric acid: light blue with carboxylic groups, khaki to dark olive with sulphonic groups) and to distinguish between basic and acid dyeing PAN fibre types (with 1% C.I. Basic Blue 3 and 1% C.I. Acid Red 151, for example from Aldrich or Ciba Erionyl Red B, 10% Glauber's salt, set to pH2 with sulphuric acid, 1–2 min at the boil).[217] Rather than relying on the rough orientation given by staining tests it would appear better to consider the fibre-specific data, in particular the rate of dyeing and the fibre saturation value, which depends on the concentration of anionic groups in the PAN fibre.[218, 219] If this data is not supplied by the fibre producer and if enough material is available it can be easily determined in the laboratory.[220] This information is also useful for clarifying cases of damage concerned with dyeing. Neal has described some methods of correction for dyeing faults with PAN.[221] If after piece-dyeing PAN is cooled down too quickly in the rope form (jet) undesired creases can be set in the cloth. A further cause of faults is excessive shrinkage, for example when dry cleaning is carried out at too high temperatures.[222, 223]

Average degree of polymerization and analysis of PAN damage

Determination of the viscosimetric degree of polymerization or simply the relative viscosity of PAN fibres can be carried out relatively easily in the solvents used for spinning such as dimethylformamide or concentrated sulphuric acid (SNV 195592 according to Schefer[113]). In this way, for example, the extent of damage after thermal degradation can be determined, especially if comparable material from the same fibre lot can be tested at the same time. Usual DP values range from 1200 to about 2000 [224] and for gel-spun PAN from 10 000 to 20 000.[213] This method is not suitable for the analysis of damage caused by hydrolysis, since this does not involve chain degradation but changes in the structure of the side groups (nitrile, ester, amide). In addition, the new side groups formed during hydrolysis (mostly carboxylic acid groups) change the viscosity of the PAN solutions and thus reduce the accuracy of the viscosimetric DP determination. More costly methods for determining DP and its distribution, such as gel chromatography, are only rarely used in exceptional cases for PAN damage analysis.

8.5.8   Analysis of damage to elastane (spandex) fibres

Elastic fibres are usually elastane fibres, which according to ISO 2076 are made up from at least 85% by weight of segmented polyurethanes. In the USA they have the generic name spandex. The definition of elastane does not include the newly developed elastic fibres on the basis of pure polyester or polyolefin.[225] Although the share of elastane fibres on the world fibre market is still less than 1% they have achieved increasingly greater importance in the last decades. In the meantime about half of all clothing fabrics contain elastane fibres and around 85% of elastane fibres are used for clothing. This increasing distribution is the first reason for the frequency of complaints relating to textiles containing elastane. The second reason is that they can be overstrained during production, dyeing and finishing and in use. This already suggests the third reason, namely the relatively high sensitivity of elastane fibres to certain types of damage. They are particularly susceptible to thermomechanical damage (by heat and tension) and are also attacked and degraded by hydrolysis (acids and alkalis) and photolysis (especially by UV light). When the conditions are not too aggressive they are stable to oxidizing and reducing agents, except for the heavy damage caused by chlorine.

The urethane link, which binds the segments of the elastane repeat units, can be described as half ester and half amide of a carboxylic acid. The stability of polyurethanes is thus similar to that of polyamides and polyesters. The latter are more stable because of their high crystallinity and compactness, which is reflected in their density (elastane 1.2–1.3 and PET 1.38 g cm^{-3}). As with all elastic substances elastane fibres are cross-linked at wide intervals. They consist of so-called soft and hard segments. The latter are the fixed points in the network, they determine elasticity (recovering force), setting and heat behaviour. The hard segments are highly crystalline and contain urethane and, in some cases, additional urea groups, both groups form strong intermolecular hydrogen bonds (cross-linking via secondary valency). The soft segments are the flexible structures with little order, located between the fixed points, and they are responsible for the extensibility. With molecular weights in the range from 1000 to 3000 they are relatively large[226] and consist mainly of aliphatic polyethers (such as polytetra-hydrofuran) or aliphatic polyesters. The former are more stable to hydrolysis whereas the latter are more resistant to oxidation (for example chlorine or photo-oxidation). The hard segments contain mainly aromatic structures which, as with the aramids, increase cohesion between the chains because of their mutual attraction. On the other hand because they absorb UV light strongly they contribute greatly to damage by light. This review is intended to show the main structural weaknesses in elastane fibres. It has already been mentioned that elastane is the fibre class with the greatest variation of types. The most important points of variation in their manufacture are:

• the type and size of the macrodiol (polyether or polyester), which makes up the soft segments;

- the type of polyisocyanate (for example diphenylmethylene and toluylene diisocyanate, MDI and TDI), with which the macrodiol is reacted and whose reaction products form the greater part of the hard segments;
- the type of chain extension, with diols extending to further urethane structures or with diamines extending to urea derivatives;
- the type of spinning process, dry or wet, reactive (chemical spinning) and, increasingly, melt spinning.

The number and association of the primary filaments to multifil yarns, the kind of thermal after-treatment (hot air, hot water) as well as the kind and amount of spinning oils varies between the many commercial varieties of elastane. Additional variety arises from further processing in the bare or covered form (elastic co-twisted, covered, core-spun or co-tangled threads). This variety can lead to mistaken identity and thus cause faults if the specific properties of each type are not given sufficient attention during processing.

Mechanical damage

Elastic multifilament yarns are less damaged during sewing than monofils because usually only a few of the primary filaments are damaged by the needle and the remainder is sufficient to hold the yarn together. Although the extensibilty at break of elastane fibres is 400–800 % mechanical damage can occur with overstretching. This does not necessarily mean that a tear occurs, large residual extension (set) and lower recovery forces can be reasons for complaint. Drastic damage includes thread breaks due to too high mechanical stress during knitting or weaving. A tear in the elastane core of a covered elastic yarn is referred to as a core break. It occurs particularly often with knitted fabrics; with woven fabrics loss of elasticity is the greater problem in practice.[227] This type of damage is easy to recognize visually. Mechanical overstraining and fatigue (ageing) can be analysed by mechanical testing methods:

- Stress/strain behaviour: a flatter form of the stress/strain curve is an indication of noticeable loss of elasticity. At higher extension the resistance of the elastane yarn increases exponentially until the thread reaches the maximum strength or extensibility, respectively, and breaks. Both values are lowered in cases of damage. As a simple manual test the extension at break can be determined as a rough guide with a scaled ruler, by measuring the initial length of an isolated section of the elastane thread and comparing with the length at break. The accuracy of this length measurement can be increased by grasping the ends of the thread with tweezers instead of with fingertips.
- Hysteresis curves: the elastic properties are determined by repeated extension and recovery at a constant rate between fixed limits (hysteresis behaviour, for example according to DIN 53835, five cycles to 300% extension). In the literature[226] extensive work on the dynamometric properties of elastic fibres and rubber threads has been cited. From their experience with many complaints

concerning elastane, Gähr and Lehr recommend that conclusions about the cause of damage should not be made from the hysteresis behaviour of an elastic thread isolated from the fabric.[227] They justify this by an extension limit of 300% in the test and by the fact that stresses which occur before the actual damage takes place can have a large effect on the hysteresis behaviour.

Thermal damage

Depending on the type of elastane fibre, noticeable thermal damage can occur when the fibres are heated above about 170 °C. Mainly yellowing accompanied by loss of strength and elasticity occurs. Under the microscope deformed elastomer fibres can then frequently be seen together with others which have taken on the contours of the covering component or adhere to it.[227] The temperature range for softening of elastane fibres lies between 170 and 230 °C, depending on the type, and for melting and commencement of degradation between 230 and 290 °C.[226] Water lowers the bonding in the hard segments (secondary valence bonding by means of hydrogen bonds); hydrothermal treatments therefore cause more damage than dry heat at the same temperature. Additional tension also increases the thermal damage considerably (thermomechanical damage). Especially if undamaged material is available for comparison damage by heat can be investigated by means of the stress/strain behaviour mentioned above or by thermomechanical methods of analysis:

• An elastane yarn set under excessive extension has a stress/strain curve lying to the 'left' of the curve for undamaged yarn. It has lower tenacity and much lower extensibility.[227]
• By determination of the hot breaking time; this is the time taken for an elastomer thread stretched by 100% to break at 193.5 °C.
• by determination of the heat distortion temperature (HDT); this is the temperature at which an elastomer thread under a pre-tension of 0.2 mN tex^{-1} and heated at a rate of 20K min^{-1} reaches an extension of 0.25%.[226]

The HDT differs greatly depending on the type of elastane fibre and often lies between 170 and 190 °C; with melt-spun fibres it can be lower. In order to avoid damage the setting temperature should not noticeably exceed the HDT of the respective elastane fibre type.[227, 228]

Marked thermal damage, leading to degradation of the polyurethane chains, can also be analysed by means of viscosimetric determination of the average degree of polymerization or the relative viscosity on which this is based. The spinning solvents dimethylformamide and dimethylacetamide[229] or hexamethylphosphoric acid triamide[113] can be used as solvents for this purpose. These viscosimetric analyses cannot be used with elastane fibres which have been covalently cross-linked and are thus not sufficiently soluble without degradation.

Yellowing after heat treatment of elastane can also be done to antioxidants in the fibre, especially of the sterically hindered phenol type.

Damage by light (photolysis)

In spite of the incorporation of stabilizers, elastane fibres are frequently damaged by light, especially when it has a high UV component (for example when wearing sport or bathing textiles outdoors). Photolysis causes discoloration as well as loss of strength and elasticity or even fibre breakage. The UV stabilizers can be partially washed out during dyeing and finishing.[226] Photolysis can be accelerated by oils and skin creams as well as sebaceous oils. The latter effect was demonstrated by Küster and Herlinger with model substances (squalene and linoleic acid methyl ester) on the basis of the decrease in relative viscosity of the damaged elastane fibres dissolved in dimethylacetamide. Perspiration, on the other hand, is said not to accelerate photolysis.[229] Küster and Herlinger list hypotheses and many citations concerning photochemical degradation. In the cases of elastane fibres based on polyether damage by light is accompanied by oxidation (photo-oxidation).

Chemical damage

Acids: elastane fibres are stable to dilute mineral and organic acids at room temperature. At higher concentrations and higher temperatures damage occurs including dissolution. The structural relationship to nylon fibres becomes apparent here, as it also does in respect to dyeing behaviour.

Alkalis: at room temperature elastane fibres are astonishingly resistant to alkalis. According to Hueber[230] it is possible to causticize and mercerize cotton/elastane blends at low temperature. At the boil, damage occurs with more than 2 g l^{-1} of soda.

Reducing and oxidizing agents: under the usual conditions of dyeing and finishing elastane fibres are relatively resistant. The limits for peroxide bleaching in blends with cotton are said by Naroska[231] to lie at pH 11 and 100 °C. The resistance to chlorinated water in swimming pools is said to be good,[226] on the other hand cases of damage have been reported. Chlorine bleach causes heavy damage, as does ozone.

Exhaust gases, especially nitrous gases (NO_x) cause damage by yellowing and loss of strength. Yellowing can also occur when nitrous gases from stenters directly heated with gas react with spinning oils, fibre lubricants and knitting oils used with elastane fibres, if these have not been completely removed by scouring.[232]

Oils and fats such as mineral oil, paraffin, wax, unsaturated fatty acids (spinning oils[228]), cosmetic oils and sun protection agents are absorbed by elastane fibres and can lead to loss of strength and elasticity due to loosening of the fibre structure. Some of these products also accelerate photolysis.[229] If dry cleaning is carried out carefully with the usual solvents such as perchloroethylene or benzene no damage occurs to elastane, except when stabilizers to light are extracted.[226] Highly polar organic solvents such as dimethylformamide, dimethylacetamide, cyclohexanone, butyrolacetone and phenols damage elastane fibres due to swelling or even dissolution.

Further types of damage, sources of faults and their detection

Many of the types of damage already mentioned are worsened in combination. Known examples are photo-oxidation and thermomechanical damage. Resistance to ageing also results from a mixture of many types of influence, for example mechanical, thermal and chemical influences such as atmospheric oxidation and the detergents and cleaning agents commonly used in laundering. The resistance to ageing of elastane fibres is much better than that of the rubber threads previously used, which were particularly susceptible to oxidation. As already described for wool, elastane fibres also appear to suffer from cumulative damage. For example, wet processing treatments during dyeing and finishing which normally have tolerable effects lead to noticeable fibre damage after intensive presetting.[228] Dyeing of polyester/elastane blends, often also with a wool component, is relatively problematical. Elastane fibres are damaged above 115 °C (as is wool also) (softening of the elastane and loss of elasticity[227]). The alternative, namely to dye with carriers at lower temperatures, is also difficult because many carriers can cause swelling of elastane fibres and thereby reduce their elasticity. During heat setting of piece goods the elastane fibre component is irreversibly damaged by too high temperatures and tension together with excessive duration (stretching without recovery).[227] Recommendations for finishing treatments for elastic textiles have been published, for example by Naroska[231] and Hueber.[230]

A frequent cause of faults is silicone stains on textiles containing elastane. During primary spinning elastane fibres require 2–6% of spinning oils,[226] this being 6 to 8 times more than on other yarns. These oils contain a large percentage of silicone oil, which in a normal pre-scour (without special detergents) is only partially removed. This is particularly a problem with cotton/elastane blends because cotton also retains a large amount of silicone. The silicone residues assist the thermomigration of dyes, which can lead to poor crocking fastness and the dyes can be deposited as stains on the fabric. Silicone stains are often first noticed after coloration and are difficult to remove. Their detection is described in Section 8.6.1.

Identification and differentiation of elastane fibres

Elastic fibres can be easily recognized on account of their elasticity. A differentiation between elastane and rubber threads is seldom necessary because rubbber threads are hardly used now. In contrast to rubber, elastane dissolves in boiling dimethylformamide. In order to clarify some cases of damage it can be important to know what type of elastane fibre has been used. Initial differentiation can be made under the microscope in the longitudinal view, and especially in cross-section, both can show large differences.[226] On account of their differing resistance to hydrolysis and oxidation it can be of particular interest to determine whether the fibre is of the polyether or polyester type. A microscopic differentiation is possible by embedding in 2 N methanolic potassium hydroxide. The ester type breaks up

Table 8.17 Test methods for damage to elastane fibres[226–228, 233]

Method	Comments
Stress/strain behaviour Also as a simple manual method for determining elongation at break	For all types of damage, especially for analysing mechanical and thermal damage. Flat form of the curve shows loss of elasticity, decrease in tensile strength and elongation at break.
Hysteresis or tensile–elastic behaviour	Loss of elasticity and residual extension (set) with almost all types of damage. During textile production modified to such an extent that this method is not recommended for analysing damage in dyeing and finishing or in use.[227, 228]
Thermomechanical analysis (TMA) and dynamic mechanical analysis (DMA)	Testing of the temperature dependence of the extension and shrinkage behaviour at low (TMA) or oscillating (DMA) yarn tension: glass temperature, elasticity and other parameters for exact differentiation of elastomeric fibres.
Heat distortion temperature, HDT	The HDT is the temperature at which a pre-tensioned elastane thread at a defined rate of heating reaches a certain extension (usually around 200 °C). Suitable for determining heat setting conditions and for testing thermal damage.
Hot breaking time	The time taken for an elastane thread stretched by 100% to break at 193.5 °C (usually > 20 s), especially suitable for analysis of thermo-mechanical damage.
Relative viscosity and average degree of polymerization	Quantitative analysis of chain degradation and degree of damage possible. Used for analysis of photo-chemical damage[229], also suitable for analysing other degradation reactions, for example by acids, alkalis, chlorine, exhaust gases or heat

within a few minutes as opposed to the ether type, where the thread structure remains.[233] Both types of elastane fibre can also be readily identified and differentiated by IR spectroscopy. The ester type is characterized by bands at 1730, 1220 and 1170 cm^{-1}, the ether type has a typical band at 1100 cm^{-1}.

Table 8.17 gives a review of the methods commonly used for analysis of damage to elastane fibres. They usually require a relatively large effort or high costs. There is a disproportional relation between the many possibilities for damage to elastane

fibres and the small number of simple detection methods known and suitable for this purpose. It would be helpful to have simple staining and solubility tests as well as microscopic methods similar to those used for studies of damage to wool, cellulosic and nylon fibres. The following methods should be tested for their suitability for detecting damage to elastane fibres:

- staining with basic dyes such as Rhodamine B, Methylene Blue and Oxycarmin. There will be greater affinity for these dyes if an increase in the number of carboxylic acid groups has occurred during damage to the elastane fibre, for example by hydrolysis of ester groups in the soft segments;
- staining with ninhydrin, which responds to amino groups, since these could be increasingly formed after damage (for example by hydrolysis or pyrolysis);
- solubility tests in dimethylformamide or dimethylacetamide, with a critical solution time (similarly to that with polyester);
- investigations by IR spectroscopy and thermal analysis, although these cannot be included under simple methods on account of the expensive instruments. However, many damage analysists have access to an IR spectrometer.

8.5.9   Analysis of damage to polyolefin fibres, especially polypropylene

Of the two polyolefin fibres polypropylene (PP) and polyethylene (PE), polypropylene has by far the greater importance. PP is the second most important synthetic fibre type after polyester and continues to grow at a remarkable rate.

PP fibres are relatively cheap. According to Schmenk and *et al.*[234] they are very resistant to acids, alkalis and organic solvents at room temperature. Damage can be caused by oxidizing substances, such as chlorine bleach and concentrated nitric acid at higher temperatures, as well as hydrocarbons and chlorinated hydrocarbons above 100 °C (swelling and dissolution). Their abrasion resistance is high. Tensile strength and extensibility can be varied within a wide range during fibre production. A great disadvantage of polyolefin fibres, which is particularly noticeable with PE fibres, is the large amount of deformation under stress, so-called creep. This is also the reason for their low degree of elastic recovery after compression, an important property with carpets. Further weaknesses are their low resistance to heat and light, especially UV light, which can lead to loss of strength. Heat stabilizers can increase the temperature for long-period thermal resistance from the usual 80 °C up to as high as 125 °C. Stabilizers to light and UV enable PP textiles to be used outdoors. Unmodified PP fibres cannot be dyed by the usual dyeing methods. Dope dyeing with pigments gives high fastness but is only economical for large quantities. For analysis of damage it is important to know that PP fibres exist in many further modifications, such as:

- those based on Ziegler-Natta catalysts (ZN-PP) or on metallocene catalysts

(mPP), the latter having a more uniform chain length and being more highly isotactic with a melting point about 15 °C lower;
- as microfibres and hollow fibres;
- antimicrobial, flame-resistant or antistatic modifications.

Recently elastic polyolefin fibres have also been introduced (generic name: lastol), they are cross-linked and stable at temperatures up to 220 °C and above.[235] High-tenacity polyethylene fibres, with ultra high molecular weight (UHMW-PE, Dyneema) have been available for some time; they are produced by a gel-spinning process at high dilution.

This review serves to illustrate that PP fibres are fairly commonly damaged by heat and light, by mechanical overstraining and long periods of strain and by oxidation, including photo-oxidation. PE fibres are even more sensitive to heat than PP fibres, but are less damaged in principle by light and oxidation. This last point is difficult to generalize about because their behaviour is strongly dependent on the type and amount of added stabilizers to light and oxidation.

Mechanical damage to polyolefin fibres

Polyolefin fibres have relatively good abrasion resistance. Their tensile strength and extensibility can be varied over a wide range by means of the chain length and draw ratio. An extreme example is high-tenacity UHMW-polyethylene Dyneema, which is used, amongst other things, for bullet-proof vests. Mechanical damage to polyolefin fibres can occur at many stages during processing and also in use. Sewing damage to PP knitted goods has been investigated by Wang *et al*.[236] Mechanical damage during needling of PP nonwovens has been described by Qian and Chu, who investigated the dynamic creep behaviour and ageing of PP geotextiles as a function of the type of bonding of the web.[237] Residual extension and deformation after longer periods of strain are also typical types of mechanical damage to polyolefin fibres. Mechanical damage can be detected by the usual physical testing methods and under the microscope, preferably in the form of surface film imprints.

Thermal and thermomechanical damage to polyolefin fibres

Low temperatures for the softening ranges of PP (150–155 °C) and especially for PE (105–120 °C) are the reason for many cases of damage caused by excessive heat, often combined with mechanical stress, that can occur in heat setting, sewing or pressing. According to Chidambaram *et al*.[238] the loss of strength in PP fibres during thermal bonding of nonwovens is due more to the temperature than to the mechanical strain. With the aid of the methods for thermal analysis (DSC, TGA, TMA, see Section 8.4.5) polyolefin fibres and their modifications can be easily identified. The melting range enables, for example, differentiation between low

density and high density PE (LD-PE and HD-PE) as well as ZN-PP and mPP. By comparing the measured value for the latent heat of fusion with the theoretical value, the purity of raw and recycled material can be determined. The degree of crystallinity can also be evaluated in this way. The stability to oxidation of PE fibres can be determined with isothermal DSC at 200 °C by measuring the time (oxidation induction time OIT) until commencement of oxidation (onset of the exothermal reaction). Buchanan and Hardegree investigated the influence of spinning conditions on the shrinkage behaviour of PP fibres by means of TMA.[180] With PE a thermal memory has also been noted, an effect which is particularly interesting for the analysis of damage. Thermal treatments cause a so-called melting gap, usually just before the DSC melting curve reaches its maximum. This effect has been explained by the fact that during thermal treatments the amorphous areas of the fibre form crystallites with a sufficiently high melting point. After complete melting of the fibre this thermal prehistory is erased, so that a comparison of the curves for the first and second run of the DSC can improve the validity of the interpretation.

Thermal degradation of PP fibres can be analysed quantitatively by viscosimetric determination of the chain length in decalin at 135 °C. More common is the determination of the melt flow index MFI, which can be carried out in an automated form.[234] The fact that marked damage is possible by thermolysis is demonstrated by the decrease in the chain length of PP granulate or PP chips to about half their initial value during melt spinning of PP fibres.[239] The molecular weight of PP fibres is given as 150 000–600 000, but usually 200 000–300 000,[234] this corresponds to an average degree of polymerization of 3600–14 300, or usually 4700–8300.

Damage by light and oxidation to polyolefin fibres, including photo-oxidation

The relatively high sensitivity of PP fibres to light and oxidation arises, amongst other reasons, from the fact that radical intermediate products are energetically favoured. The methyl groups on the tertiary carbon atom are weak electron donors. They thus stabilize free electrons on the tertiary C atoms. Cleavage by radicals of the C–H bonds of the tertiary C atoms is thus favoured. The necessary activation energy can be supplied by heat (thermolysis), light (photolysis) or by reaction with free radicals. In the presence of oxygen, peroxide radicals are formed at the tertiary C atoms in the chain. These react with other tertiary C–H groups, forming hydroperoxides and new PP radicals. The hydroperoxides decompose with chain cleavage, whereby carbonyl and alkene structures are formed.[240] Heat stabilizers are radical catchers, for example sterically hindered phenols or phenol-free compounds. Phosphites, for example, which reduce the peroxides, are used as antioxidants. Hindered amine stabilizers, HALS, can be used as UV stabilizers.[234]

The above-mentioned types of damage are manifested by chain degradation and yellowing, accompanied by brittleness and loss of strength. They can be detected

and analysed by the appropriate methods described in the two preceding sections. However, loss of fibre strength often does not correlate with viscosity or chain length. Martin explains this by the supposition that with damage by light the amorphous areas are preferentially degraded.[241] Pezelj *et al.*[242] have investigated damage to PP fibres by ozone and light, whereby low concentrations of ozone sufficed to cause brittleness, loss of strength and increase in hydroperoxide content.

Hydrolytic damage to polyolefin fibres

Because of the continuous carbon chain and the lack of sensitive side and end groups, polyolefin fibres are particularly stable to hydrolysis. They are stable even at extreme pH values, if other factors are not involved. Thus PP is soluble in hot, concentrated nitric acid because it also acts as an oxidizing agent. Polyolefin fibres are not soluble in cold concentrated sulphuric acid (that is, at room temperature). The solubility groups developed by Stratmann[8] for the identification of fibres (SG I to VI, see Table 8.18) clearly show the differing resistance to acids of the fibre types. Only SG I is an exception. Here, the cellulose fibres, which would interfere with a further division according to increasing acid stability, are identified with cuoxam. Cellulose acetate and nylon fibres, which already dissolve in glacial acetic acid, are relatively sensitive to acid (SG II). Acrylic fibres need cold concentrated nitric acid to dissolve (SG IV). Even more resistant to acid is polyester, which dissolves in cold concentrated sulphuric acid (SG V). All types of fibres which are not soluble in this acid are grouped together in SG VI. Here the polyolefin fibres can be found together with chlorovinyl fibres and polytetrafluoro-ethylene, which all have a continuous carbon chain and acid-resistant substituents.

Further types of damage to polyolefin fibres

Polyolefin fibres are themselves very hydrophobic and therefore absorb hydrophobic substances such as oils, greases and waxes. The intermolecular bonding, which is not very strong in the first place, is decreased further, leading to a loss of strength. A number of organic solvents also cause damage by swelling or dissolution, although these generally only take place at higher temperatures (> 100 °C). Formation of clumps with PE and PP fibres, without complete dissolution, occurs with boiling dimethylformamide, cyclohexane, γ-butyrolactone, benzyl alcohol, phenol and *m*-cresole. Both polyolefin fibres are dissolved by boiling tetrachloroethylene and tetrachloromethane, mono- and dichlorobenzene, amyl acetate, toluene and xylene.[8] In this way PP contamination (packing material) can be dissolved out of wool with perchloroethylene at 115–118 °C. After repeated dry cleaning with perchloroethylene or laundering, PP textiles show increasing ageing and an increased content of peroxide groups, probably caused by washing out of stabilizers.[242] Chlorine damage to PP fibres is also known, for example

Table 8.18 Classification of manufactured fibres in solubility groups (SG) according to Stratmann[8, 123]

SG	Solvent	Type of fibre	Abbreviation
I	Cuoxam (under the microscope)	Cellulosics	CO, CV, CC, CD, CLY
II a	Glacial acetic acid, cold	Diacetate, triacetate	CA, CT
II b	Glacial acetic acid, boiling	Aliphatic PA (nylon) fibres, polyurea, poly (lactic acid)	PA 6, PA 6,6, PA 4, PA 11, PA 12, PUA, PLA
III	6 N Hydrochloric acid	Vinylal fibres (polyvinylacetal)	PVA+
IV	conc. Nitric acid	Acrylic fibres, poly-(phenylene sulphide) (elastane fibres usually disintegrate, Tohalon dissolves)	PAN PPS EL (PUE) CT (Tohalon)
V	conc. Sulphuric acid, cold	Polyester with modifications	PET, PES(V), PES(G), PES(A), PES(K), PEN, PTT, PBT
		m-aramid, polyimide, poly(ethylene naphthalate), polyetherketone, poly(glycolic acid), some multipoly-merisate fibres and alginate	*m*-AR PI PEN PEK PGA PVM(V), PVM(D), AL
V and VI	Partially soluble in cold conc. sulphuric acid	*p*-aramid, polybenzimidazole, Kynol, Tenax, Kermel	*p*-AR, PBI
VI	Insoluble in the solvents of SG I to V	Polyolefin fibres, polytetrafluor-ethylene, chlorovinyl fibres, multipolymerisate fibres, polycarbonate fibres, modacrylic, fibres from regenerated proteins	PP, PE PTFE PVC, PVC+, PVD PVM(D), PVM(Ac) PC MAC, PAM e.g. KA

Ulmann has described damage caused by sodium hypochlorite, whereby the strength decreased markedly and the PP fibres were no longer soluble in decalin.[243] Damage to PP fibres by aerial pollution was investigated by Cunko and Pezelj, whereby strength and isotacticity decreased, even without the effect of light, and the content of hydroperoxide groups increased.[244]

Unfortunately there are not enough simple methods of detection of damage to

polyolefin fibres. On the other hand there are also not so many cases of complaint, based on damage to PP and PE fibres, which are difficult to analyse, although these fibres are increasingly present in all three segments of the textile market. They are particularly important in the field of technical textiles, including nonwovens (for example hygienic, agricultural, building, industrial, protective and medical textiles, geotextiles, vehicle interiors, packing materials, filters, ropes) but also in home furnishings and household textiles (carpets, furnishings, bathroom accessories, cleaning cloths). They are also to be found in some clothing areas (for example sportswear, functional underwear, socks).

8.6   Special types of damage and their analysis

As a supplement to damage analysis in relation to specific fibres this section deals with important types of causes of damage. Mahall divided his book[5] entirely on the basis of types of damage, namely:

• chemical damage
• mechanical damage
• thermal and thermomechanical damage to synthetics
• streaks and bars in textile fabrics due to yarn differences and technological reasons
• causes of the formation of tight threads and their effects
• defects caused by deposits and encrustations on the fibre material
• other defects in the quality of textiles
• microbiological damage to fibres.

If the titles of this book *Chemical Testing of Textiles* and this chapter 'Chemical analysis of damage to textiles' are taken narrowly only chemical types of damage and chemical testing methods for other types of damage should be discussed here. But there is no clear-cut borderline and a too narrow treatment would not do credit to the broad subject of chemical analysis of textile damage. Thus, for example, technological faults due to using mistaken material or caused by foreign fibres can often be most simply clarified by chemical identification of the fibres. In practical damage analysis, physical methods are often combined with chemical ones, for example microscopic staining, swelling and dissolution reactions or colour reactions and derivatization in chromatography. IR spectroscopy, a physical method, requires chemical knowledge for the identification of fibres, textile auxiliaries and stains. The selection of special types of damage causes described here is restricted to the investigation of deposits on fibres, especially stains, the detection of the causes of streaks and barriness, and to biological damage.

8.6.1 Analysis of unwanted deposits on textiles

Since these deposits are usually not distributed evenly on the fibres and textile

fabrics they often consist of more or less large stains, spots or streaks. They are one of the most frequent causes of damage (see Section 8.3.3). Deposits of lime or PET oligomers show up as greyness on white fabric or light-coloured structures on dyed fabric. The identification of PET oligomers is described in Section 8.5.5. Lime is soluble in acid and can be washed off with, for example, acetic acid or sequestering agents. Calcium ions can be detected by precipitating them as oxalate.[7] Mahall has described a simple microscopic detection method for lime.[5] The textile sample is ashed and the residue taken up in a little 2 N hydrochloric acid. A small drop of this solution is placed on a microscope slide and next to it a small drop of 2 N sulphuric acid p.a. is placed. A cover slip is then laid carefully over both drops. If lime deposits are present needle-shaped crystals of calcium sulphate can be seen in the mixed liquids under the microscope.

Detection of oil, grease, paraffin and wax deposits

These hydrophobic substances can often be marked and detected by staining with oil dyes. Mahall[5] and others recommended the oil dyes Sudan Red 460 and Sudan Red 7B (C.I. Solvent Red 19), Fat or Oil Red 5B (C.I. Solvent Red 27) and Duranol Blue PP (ICI). Nowadays Sudan Red 7B and C.I. Solvent Red 27 as Oil Red O are available both from Aldrich and Fluka. According to Mahall about 1 g l^{-1} of oil dye is used to prepare the oil dye reagent for macroscopic tests. The dye is first stirred with 10 ml methanol for about 3 min, water warmed to 40 °C is then poured over this and 10 ml of concentrated hydrochloric acid is added. The sample under investigation is treated for about 10 min at 40 °C with this reagent, if staining is faint the time can be lengthened or the temperature increased to 70 °C. It is recommended that a flat vessel be used in which the sample is not pressed or creased. The sample is then rinsed thoroughly for 3 min under running water and dried at a maximum of 100 °C. Oily deposits can then generally be distinctly seen on account of their coloration. For microscopic investigations it is recommended that a solution of 3–5 g of oil dye in 50 ml ethanol, to which 50 ml of glycerine is added, be used as an embedding agent. In this way, oil or grease contamination which has diffused into the fibre (for example into PET or PP fibres) can be seen.[5] A similar recipe for microscopic detection of oils was given by Bigler:[13] three parts by volume of alcohol and one part water are mixed and saturated with oil dye. One part by volume of glycerine is then added to this solution. Peter[24] modified this recipe by doubling the amount of glycerine.

Even more sensitive than these staining tests for detecting grease and oil contamination is an imprint on thermoplastic films (see Section 8.4.6). During production of the imprint, hydrophobic deposits diffuse into the film and can usually be easily recognized by the local cloudiness they cause. The natural waxes of cotton do not interfere here because they are evenly distributed. Spots caused by pigments or disperse dyes are also transferred onto the film imprints and are then easier to investigate microscopically.[5]

In addition, grease, oil, waxes and paraffins can be detected by IR spectroscopy, either by a direct comparison of spectra from the stain and from unstained areas, with the possibility of subsequent subtraction of spectra, or after extractions and concentration by spectroscopy of the extraction residue.

In the latter case it is also recommended that extracts from a stained area be compared with a similarly sized area without stains. Long alkyl chains are characteristic of these compounds, which can thus be identified, for example, by the intensive C–H bands just below 3000 cm^{-1}. Apart from these stretching bands, intensive deformation bands at about 1500 cm^{-1} and a weaker band at 720 cm^{-1} are also found, the last one being characteristic of a chain structure with more than three methylene groups. The extracted fats and oils can also be analysed more exactly by thin layer chromatography (see Section 8.4.3). An indication of oil deposits is given by fluorescence in UV light[43] on the fabric (if it has not been optically brightened) as well as in the extraction residue and on the TLC plate.

Detection of unwanted film-like deposits

This kind of deposit interferes by causing, for example, a harsh handle, dye reservation or other optical effects, and also chalky streaks when the fabric is scratched. Typical causes are size residues, printing paste thickeners which have not been washed off or unevenly distributed finishing agents. They can usually be identified with the aid of film imprints, since they often show up in the form of flat cakes or crumbly deposits.[5] Film-like deposits usually cause a somewhat blurry appearance of the surface imprint, for example blurred scale structures in wool. Size residues can be detected by colour reactions on the fabric or in an extract (combined with precipitation reactions).[245] An advantage of the imprint method here is that the textile fabric can be investigated without being separated into individual fibres, which would destroy film-like deposits. However, deposits can sometimes be better analysed by means of staining tests and the preparation of cross-sections of yarn or fabric. Mahall[5] investigated fibre adhesion and size residue (including distribution of size and over-sizing) in this way.

Detection of other deposits in the form of stains

The high frequency of stains as a manifestation of damage was mentioned in Section 8.3.2. The reasons for the occurrence of stains are very numerous. Several examples of stain analysis were described in Section 8.4.4 and the typical method of approach in Section 8.3.5. Löffel[74] has also described the comparative selective extraction of stains with subsequent identification, preferentially with TLC and IRS. In Section 8.4.3 details of TLC analysis of stains caused by grease and oil or polyester carriers are presented. In Section 8.4.4 information is given on the identification of silicone stains and fluorocarbon deposits using IRS. The detection of silicones with fluorescence microscopy is described in the literature.[42]

Table 8.19 Types of stain and the processing stage where they occur[3]

Occurrence	Type of stain and cause
Production of yarns and fabrics	Oil and paraffin stains (usually wet paraffinizing), often together with abraded metal, which darkens the stain Small spots due to fly and clumps of foreign fibres
Pretreatment	Residues of size (usually widely distributed on the warp, blurry warp streaks) Residues of sizing auxiliaries such as paraffins, oils, waxes, fats, softeners and smoothing agents Preserving agents (often inhibit enzymes) Silicone stains from antifoaming agents Acid and alkali stains
Dyeing	Antifoam stains based on mineral oils or silicones, sometimes also containing silicic acid (see Section 8.4.4) Stains caused by PET carriers and oligomers Precipitation of auxiliaries with opposite charges Lime and phosphate deposits Spots due to undissolved or precipitated dye Stain-like lighter dyeing due to air bubbles in wound packages Stains due to drips of water or chemicals (change in dye affinity)
Finishing	Silicone stains (often darker, from softening, stretch or hydrophobic finishes and antifoaming agents) Softeners, hydrophobic agents, flame retardants and other finishing agents which have precipitated due to faulty treatment conditions, usually colourless and uncommon
Storage and transport	In addition to soiling, stains due to yellowing, caused by antioxidants in plastic films and cartons together with nitrous oxides in the air (combustion engines) and cationic substances[246]

Schindler *et al.*[3] have published a comprehensive review of the relevant literature and of types and causes of stains formed during production and dyeing and finishing of textiles (see Table 8.19). In this review the fibre-dependent limits of detection by IRS of stains caused by mineral oil and paraffin, sizes based on polyacrylate, fabric softeners and polyester carriers are described. Stains which arise during textile usage are often easier to analyse because the circumstances of their occurrence are mostly known or are fairly easy to determine.[247] Illing-Günther and Hanus have described a stain analysis with microspectrophotometry.[37]

   As well as the most common form of stain, namely that caused by deposits of foreign substances, there are two further kinds. One occurs owing to localized effects of chemicals which modify the fibres in such a way that they reflect light or take up dye differently, for example splashes of caustic soda on cellulose. For the

detection of this chemical damage the fibre-specific methods of analysis described in Section 8.5 can be used. In addition, residues of the chemical which caused the stain can sometimes be detected directly on the fabric or in an extract. With the third type of stain arising as a result of mechanical influences, the local reflection of light is modified in such a way that a manifestation of damage in the form of a stain occurs. This can best be detected under the microscope, for example by starting with a stereomicroscope and different types of illumination.

Identification of the substances which caused the stain is usually the prerequisite to determining who is responsible, who carries the blame and how best to repair the damage. Optimal removal of the staining substance requires knowledge of the fibre involved in order to avoid further damage to the textile during stain removal. As a rule small individual stains are removed by stain removing agents. With larger or more frequent stains, dry cleaning or scouring, depending on the type of stain, is carried out with possible addition of surfactants, sequestering agents, enzymes, acids or bases.

8.6.2   Detection of the causes of streaks and barriness in woven and knitted fabrics

Streaks and bars are second only to stains as one of the most common manifestations of damage. They occur in numerous forms,[248] for example:

- parallel or oblique to the warp or weft direction
- with a repeat pattern or irregularly
- in bands or bars
- running along short or long sections of thread or across differing numbers of wales or courses.

The cause of the fault can usually be clarified here with the aid of a microscope and film imprint. The causes are as numerous as the forms the faults take. This is illustrated by the 24 relevant examples in Mahall's book[5] and the 10 examples in Goebel's publication on the formation of streaks.[248] As a rule streaks and bars are caused by faults in textile production. Examples of this are:

- mistaken material, usually use of the wrong yarn
- differences in yarn count, yarn bulk, yarn twist, thread tension, plying, pile opening, hairiness, inhomogeneous blends
- faults during texturizing or mercerizing
- with pile fabrics, more deeply incorporated tuft rows or differences in needling.

Faults arising from dyeing and finishing are also known:

- wet abrasion and other types of mechanical damage in jet dyeing machines
- plaiting-down faults in cotton pretreatment: squashed fibres, notches, cracks and splits in the fibres which occur when the goods, swollen with alkali, are packed down too densely

- greasy deposits and resinated mineral oil, which have a carrier effect on polyester, leading to deeper dyeing.

8.6.3   Detection of biological damage

As well as damage to wool by the larvae of clothes moths and carpet beetles, as discussed in Section 8.5.2, microbiological damage to fibres is of interest here. This damage is usually caused by fungi and, less commonly, by bacteria. Bacterial damage to wool is known to occur, it causes fibre degradation and an unpleasant odour. Bacteria often live in symbiosis with fungi on fibres. Both types of microorganism can feed on natural fibres and many types of textile auxiliary based on natural substances, for example sizes, spinning oils, fabric softeners, starching agents and stiffening agents, printing paste thickeners and other types of digestible agents. Synthetic fibres are not completely resistant to microorganisms, for example elastane fibres and polyurethane coatings can be damaged by them. Humidity, warmth and time favour microbial damage. It leads to loss of strength and occasionally to mildew stains, unpleasant handle, odours and loss of colour. Microbial damage frequently occurs after lengthy transport of goods packed when damp or containing size, or when damp fabric is stored overnight or over a warm weekend in a textile dyeing and finishing mill. Antimicrobial treatments can prevent such damage but it still occurs repeatedly in practice.

Musty smelling mildew stains are often a first indication of fungal attack. They occur particularly frequently on cellulosic textiles and their colour varies depending on the type of fungus, from black to olive green, reddish brown to orange and yellowish brown. According to Nopitsch[249, 250] actual detection of the fungus is best made under the microscope by staining with Lactophenol Blue reagent. The Cotton Blue dye, which gave this reaction its name, is no longer available. This is also the case for the replacement dyes Water Blue B[13] and Lanaperl Blue RN 150[5] (C.I. Acid Blue 281). Mahall[5] recommends the still available substitute Telon Blue AGLF (DyStar) and in addition he mentions a 0.5% solution of Methylene Blue as a possible alternative.

Preparation of the Lactophenol Blue reagent: Solution A consists of 20 ml of lactic acid, 20 g of phenol, 40 ml of glycerine and 20 ml of distilled water. Solution B consists of 2 g of dye in 100 ml of distilled water. The reagent is prepared by mixing 50 ml of solution A and 10 ml of solution B.

Method for Lactophenol Blue staining: several fibres from the sample are cut to a suitable size, embedded directly in the Lactophenol Blue reagent and covered with a cover slip. Since the reagent itself is dark blue the stained mycelium threads and spores of the fungus cannot always be easily recognized. For this reason after at least 10 min and up to a maximum of 30 min the reagent solution is sucked out by a strip of filter paper (rider) bent upwards in the middle, which is placed at the side of the cover slip. At the same time drops of solution A are placed on the opposite side of the cover glass so that the sample does not dry out. This rinsing

treatment, which increases the colour contrast, is critical because if the solution is drawn through too quickly fragments of the fungus can be washed away. On the other hand the blue-stained mycelium threads and possible spores and bacteria colonies only become clearly visible after this rinsing treatment. This detection method becomes more difficult and requires much patience and preparative skill if the sample under investigation was washed after the microbial attack, so that only traces of the microorganisms can be found.

Mildew stains can be removed by intensive bleaching. Previously, chlorine bleach was regarded as the best method for this with many types of fibres, except wool, silk, nylon and elastane. Overdyeing to black was the only solution for fibres sensitive to chlorine. In all cases the more or less marked loss of strength, depending on the degree of damage, remained a problem. In Mahall's book[5] there are many well-illustrated practical examples of fungal damage and also three examples of bacterial attack on wool. To analyse this type of damage to wool, the book by Doehner and Reumuth[150] can also be recommended.

Bacterial damage to wool is also favoured by warmth, humidity and time. A neutral to weakly basic environment supports bacterial growth; low pH values inhibit it. Level souring-off of the fabric is the simplest method of protection against bacteria when wool has to be stored moist for longer periods of time. With wool not only the fungi and bacteria cultures are stained with the Lactophenol Blue reagent but also the damaged areas of the wool are clearly and specifically more deeply stained. This is helpful in damage analysis when the actual microorganisms have been washed out during scouring. In bacterial damage, longitudinal striations first appear on the wool fibre and the spindle-shaped cells of the orthocortex are then laid bare. This results in a characteristic appearance of bacterial damage.[5] Only after further, more extensive damage are the spindle cells of the paracortex laid bare, since these contain a greater concentration of stabilizing disulphide links. Since wool is also fibrillated by acid damage, it is recommended that this be differentiated from bacterial damage by carrying out the KMV reaction with ammoniacal potassium hydroxide (see Section 8.5.2). Macroscopically, stains caused by bacterial attack appear lighter because the fibrillation leads to a greater scattering of incident light.

8.7   Special applications and particularities of textile damage analysis

8.7.1   Forensic application of textile damage analysis methods

Forensic science and its application in criminal investigative technology are used to help clarify criminal cases. Textiles can play an important role here, usually in the form of clothing but also including household and automobile textiles, furnishings and in rare cases also technical textiles, for example strings and ropes used to

bind, strangle or hang victims. Textiles used by criminals can also include stocking masks, gloves, bags, sacks or adhesive tapes. Sometimes it is possible to solve cases of murder unequivocally with the aid of a few typical fibre traces transferred from the murderer to the victim and/or vice versa.

Although the aims and tasks of textile damage analysis are usually less dramatic, the methods used are often the same as those in textile-related criminal investigative technology. For this reason, colleagues from the German Federal Criminal Bureau have been present at all the Münchberg symposia on textile damage analysis. An important difference from textile damage analysis is that in criminal investigations there is often very little fibre material available. In addition, most of this material has to be retained unchanged as evidence and possibly as material for a further expertise. Therefore, in such cases non-destructive methods of identification and further analysis are preferred. Dissolution, melting, staining and so on are only permissible when larger samples are available. Microscopy with its many modifications such as comparative, polarization, interference, fluorescence, thermo- and FT-IR microscopy play a dominant role as well as microspectrophotometry and scanning electron microscopy with energy dispersive X-ray spectroscopy.

In order to identify fibres non-destructively by polarization microscopy the birefringence is determined.[35, 36] This is based on the refraction of polarized light in the crystalline areas of the fibre. The birefringence is the difference between the refractive index parallel and the refractive index perpendicular to the fibre axis. For this method of fibre identification the birefringence is determined more easily via the retardation, using a Michel-Lévy Colour Chart. In this chart the retardation and the birefringence are plotted against the fibre thickness. For each type of fibre a straight line approximately passing through the origin and with a characteristic slope is obtained. Less common and more costly, but more accurate for criminal investigations, is the identification of fibres by interference microscopy. Here the refractive indexes of the fibre are determined parallel and perpendicular to the fibre axis. The unknown fibre can then be localized in a plot of these refractive indexes, where it can be identified by its correspondence to the values for known fibre samples.[251] Especially fine differences in crystallinity due to different speeds during spinning of polyester fibres can be detected by interference microscopy.

The methods mentioned above show that the effort required for cases of criminal investigation can be considerably greater than that for the usual analysis of damage to textiles. Both fields have the problem of obtaining representative samples. In damage analysis this will determine how conclusive and representative the detection of the damage or the specific changes in the fibres from the case in hand will be. Since there will always be a few stray fibres, sometimes as many as 100 samples have to be investigated in order to obtain a representative picture. This question of the strength of evidence based on a few investigated fibres is even more critical in criminal investigations because the result of the investigation is often the basis for the court's verdict. Therefore it has to be perfectly clear whether typical fibres, for example from the victim's or suspect's clothing, have been unequivocally

detected on a certain piece of evidence. From the many kinds of transferred fibres certain target fibres may be selected as evidence, such as:

- those with special properties (colour, type of polymer, morphology),
- synthetic fibres, which usually produce more solid evidence than natural fibres,
- fibres which are very easily transferred and can also distribute themselves in the environment of the victim or suspect,
- fibres which are to be found in the most relevant places (for example underwear in cases of rape).[252]

It is essential for the court to know how highly the results based on fibre traces are to be rated as evidence. In order to assess the evidential value of transferred fibres their frequency has to be taken into account as well. This so-called degree of discrimination is obtained from studies on fibre population (frequency of occurrence at certain places or on certain objects) and from databases, which, for example, give information about the frequency of certain types of fibres in the relevant types of clothing.

It is also interesting in damage analysis to know which fibre characteristics are determined in criminal investigations. Typical characteristics are:

- the morphology, such as length and thickness and their distribution, fine structure and cross-sectional shape,
- then the chemical basis, including possible types of modification, especially with acrylic and polyurethane copolymers,
- the degree of delustring including the particle size and distribution of these pigments,
- the state of finishing, including method of coloration and type of dyes and finish,
- characteristics of textile care such as wet laundering or dry cleaning,
- typical traces of use such as wear, ageing and soiling.

The variety of available methods of investigation is usually greater for synthetic fibres than natural fibres. With cotton and wool an exact allocation is often only possible on the basis of their dyeing, which is analysed on single fibres using a microspectrophotometer, with similar results to colour measurements in a textile mill. If the amount of sample is a little larger the dyes are also identified by means of TLC and HPLC. Thus, in the case of a murderer who had used a red acrylic scarf it was not only possible to determine the scarf manufacturer and the dyeing mill but also to show that the dyeing recipe used for the suspect's scarf and that for the sample scarf used for comparison were different.

A special case of fibre identification involves vehicle accidents with fatal injuries to the occupants. The high pressure of impact causes such a high frictional heat that fibres are embedded in plastic surfaces which are momentarily softened and the fibres are retained there after the plastic cools down. With these traces, known as fusion marks, it is possible to reconstruct where the passengers were

sitting and to determine who was driving. Fibre traces on the seats are not so conclusive because they can have gathered there over a longer period of time.

The criminal investigator attempts to use the characteristics of fibre traces and their environment to obtain a degree of certainty as great as possible for the evidence of fibre transfer and its conclusiveness and, in the long run, whether with this evidence the suspect can be found, incriminated or exonerated. Extensive literature is available on forensic analysis, for example from Grieve.[59, 253, 254]

8.7.2   TESS, an expert system for textile damage analysis

Another particularity of textile damage analysis is the expert system TESS. This abbreviation stands for Textiles Experten-System für Schadensfälle (Textile Expert System for Cases of Damage). It will be briefly described here because this enables an interesting survey of the method of approach and uses of such systems as well as giving an idea of the complexity and problems of damage analysis in textiles. TESS was developed from about 1993 by the Eidgenössische Materialprüfungs- und Forschungsanstalt (EMPA) in St. Gallen, Switzerland, in close cooperation with a dozen project partners and has been in industrial use since 1998.[255–258]

TESS is a Windows-based diagnostic system for all stages of textile production including dyeing and finishing. The knowledge gained from numerous experts was continuously structured and implemented in a knowledge base. This consists of a network of about 2000 nodes. The initial nodes of the network are five simplified manifestations of damage (stains, streaks, holes, surface differences and differences in handle). These are further sub-divided according to size, direction, frequency, colour and position of the fault. For an exact determination of the cause of the damage further investigations are requested, for example observation of the fault in reflected and transmitted light and possibly UV light, surface film imprint, determination of whether the fault runs parallel to the threads, determination of count and fastness or extraction. In the form of a dialogue TESS suggests further stepwise tests, delineates the area of possible causes and, if successful, names the cause of the fault and ways to repair it and avoid it in future.

Further advantages of TESS are that it supports and relieves experts during damage analysis, and is especially useful in training new staff. It is always available, it considers very many possibilities and notes the steps taken (transparent logic). It serves to preserve the specialized knowledge of experts who retire and sometimes enables shorter diagnosis times and earlier recognition of the cause of faults. Disadvantages of TESS are that until now it has mainly been successful with faults arising from textile production and it appears to be limited in its suitability for the numerous types of damage connected with textile dyeing and finishing. In spite of the large amount of work invested in its development, much more experience has to be included. Since this continuing effort appeared to be too time-consuming and expensive, further work on this difficult project ceased in 2002. In

the long run TESS was not able to cope with the enormous variety of cases of damage in textile dyeing and finishing, the complexity of the manifestations of damage and, in particular, their causes. On the other hand this emphasizes the importance and illustrates the performance of experienced damage analysts.

8.8   Concluding remarks

The previous section again shows the great variety and complexity of damage analysis on textiles in general and textile chemical damage analysis in particular. These challenges correspond to the demands made on damage analysts in terms of broadly based, thorough knowledge, great experience and the right combination of logical and intuitive approaches depending on the problem at hand. In addition, these experts require many kinds of information, not only concerning the particular case of damage but also on approaches and solutions to similar cases. Private collections of cases of damage, study of the literature and exchange of ideas with colleagues are always helpful. Useful ideas (sometimes generated just by aside comments), that help in interpreting one's own work can arise while reading the many published cases of damage in practice. Well-known experts have described in these publications their often very individual approaches based on their particular experience in analysing textile damage. Occasionally they are honest enough to confess that in spite of much effort a case could not be solved under the given circumstances. Compared to this, the results of a database research on damage analysis of textiles were rather disappointing. Only a small percentage of the finds proved to be useful. Presumably the choice of keywords when preparing the abstracts was not sufficiently adapted to the contents and questions which are of interest here.

   Many interesting details of the published examples of damage analysis did not fit into the structure of this comprehensive chapter, in particular they did not fit into the division into methods and damage analysis in relation to the type of fibre. In conclusion, reference is again made to the analogy used in the introduction to this chapter: by reading this chapter the temple-like structure and in particular its roof may have become more familiar to the reader and it is hoped that the foundations and columns have been sufficiently reinforced so that the ponderous roof now appears somewhat lighter.

8.9   Acknowledgments

8.10   References

1 Peter U, Ciba, paper presented at the University of Applied Sciences at Münchberg, June 1993.
2 Losch M, Forschungsinstitut Hohenstein, *7th Symposium on Textile Damage Analysis*, Münchberg, March 1998.
3 Schindler W, Müller P and Pehl F, 'Infrared spectroscopic identification of stains produced on textiles during manufacture – a comparison on methods, Infrarotspektroskopische Identifizierung von herstellungsbedingten Flecken auf Textilien – ein Methodenvergleich', *Melliand Textilberichte,* 1992, **73,** 514–521.
4 Schindler W, 'Textile Qualitäts-, Schadensfall- und Fremdmusteranalyse mit einfachen IR-Methoden, Teil 3: Einfachreflexions-Diamant-ATR', *Melliand Textilberichte,* 2004, **85,** 278–280.
5 Mahall K, *Quality Assessment of Textiles – Damage Detection by Microscopy,* 2nd edn, Berlin, Springer, 2003.
6 Hearle J W S, Lomas B, Cooke W D and Duerden I J, *Fiber Failure and Wear of Materials,* Chichester, UK, Ellis Horwood, 1989.
7 Agster A, *Färberei- und Textilchemische Untersuchungen,* Berlin, Springer, 1967.
8 Stratmann M, *Erkennen und Identifizieren der Faserstoffe,* Stuttgart, Spohr-Verlag, 1973.
9 Greaves P H and Saville B P, *Microscopy of Textile Fibres,* Oxford UK, BIOS Scientific, 1995.
10 *Identification of Textile Materials,* 7th edn, Manchester, UK, The Textile Institute, 1976.
11 Stratmann M, 'Identifizierung der Faserstoffe', *Deutscher Färber-Kalender,* 1970, **74,** 514–534.
12 Stratmann M, 'Mikroskopisch erkennbare Fehler und Schädigungen an Textilfasern', *Deutscher Färber-Kalender,* 1972, **76,** 480–493.
13 Hemmpel W-H, 'Fehler in der Farbgebung-Nachweismöglichkeiten für den Praktiker', *Textil Praxis International*, 1983, **38**, 1329–1332, 1337, 1338, 1340, 1342.
14 Hemmpel W-H, 'Gewährleistungshaftung – Produkthaftung – Umwelthaftung – drei wichtige Gründe für die Qualitätssicherung', *Textil Praxis International,* 1991, **46,** 130–132, 134–137.
15 Hemmpel W-H, 'Reklamation des Endverbrauchers an Färber und Appreteur – verdeckte Mängel im Textilgut', *Textil-Betrieb,* 1983, **101,** 22–26.
16 Lancendorfer T, 'Möglichkeiten der Mikroskopie bei der Qualitätsbeurteilung und Fehlererkennung an Fasern und Flächengebilden', *Melliand Textilberichte,* 1990, **71,** 493–497.
17 Kunze W, 'Reklamationsfälle aus der Veredlungsindustrie und ihre Ursachen', *Textil Praxis International,* 1974, **29,** 315–324.
18 Schefer W, 'Schädigungen von Wolle durch Veredlungsoperationen', *Textilveredlung,* 1980, **15,** 484–487.
19 Pehl F, 'Fehler in Textilien und die Ermittlung ihrer Ursachen – Schadensfälle aus der Textilindustrie', *Taschenbuch für die Textilindustrie,* 1984, 415–429.
20 Various authors, Vom Textillabor zur Textilpraxis, Schweizerische Vereinigung von Färbereifachleuten, SVF, Basel.
21 Anonymous, SVF-Lehrgang für den Textilveredler, S 1 – S 107, Schweizerische Vereinigung von Färbereifachleuten, Basel, 1967–1969.
22 Bigler N, Die Erkennung von Fehlern in Textilien, CibaGeigy AG, Basel.
23 Anonymous, Schadenfälle in der Textilindustrie, Ciba AG, Basel.

24 Peter U, *Schadenfallerkennung – Mikroskopische und chemische Methoden,* 2nd edn, Basel, Ciba-Broschüre 9287/27.713, 1993.

25 Wurster P, Schmidt G *et al.*, 'TEGEWA-Tropftest', *Melliand Textilberichte,* 1987, **68,** 581.

26 Stratmann M, 'Hochtemperaturfasern und ihre Identifizierung', *Melliand Textilberichte,* 1982, **63,** 215–219.

27 Rossbach V and Leumer G, 'Qualitative Faseranalyse: Identifizierung von technischen Spezialfasern', *Melliand Textilberichte,* 1988, **69,** 351–360.

28 Reiter K, 'Mikroskopische Identifizierung von Regeneratcellulosefasern', *Taschenbuch für die Textilindustrie,* 2000, 172–179.

29 Ulmann E, 'Unterscheidung der gebräuchlichen Synthesefasern mit Hilfe von Lösungs-Reaktionen unter dem Mikroskop', Sonderdruck (offprint of) der EMPA St. Gallen aus Mittex 1/1981.

30 Reumuth H, 'Textil-Mikroskopie, Teil II', *Zeitschrift für die gesamte Textilindustrie,* 1961, **63,** 3–9, 82–89.

31 Koch P-A, *Mikroskopie der Faserstoffe,* Stuttgart, Spohr-Verlag, 1972.

32 Loske T, *Methoden der Textilmikroskopie,* Stuttgart, Kosmos Franckh'sche Verlagshandlung, 1964.

33 Bigler N, 'Einige mikroskopische Methoden zum Nachweis von Fehlern in Textilien', *Textilveredlung,* 1975, **10,** 134–150.

34 Schmidt G, 'Schäden an Web- und Maschenwaren aus Mischgespinsten – Prüfung mit mikroskopischen und anderen Methoden', *Textilveredlung,* 1974, **9,** 59–66.

35 Schmidt G, 'Mikroskopie im Textilbetrieb', *Taschenbuch für die Textilindustrie,* 1993, 458–470.

36 Zschach S, 'Lichtmikroskopische Verfahren bei der Untersuchung von Faserstoffen', *Taschenbuch für die Textilindustrie,* 2000, 190–204.

37 Illing-Günther H and Hanus S, 'Textilmikroskopie – Untersuchungsverfahren für Fasern, Fäden und textile Flächen', *Taschenbuch für die Textilindustrie,* 2000, 180–189.

38 Kunze W, 'Untersuchungen von Färbereiproblemen mit Hilfe der Mikroskopie', *Melliand Textilberichte,* 1973, **54,** 1077–1081.

39 Nettelnstroht K, 'Schadensuntersuchung im Textilbetrieb mit dem Polarisations-mikrokop', *Melliand Textilberichte,* 1983, **64,** 918–921.

40 Schmidt G, personal communication and *Textilien unter dem Mikroskop*, paper presented at the University of Applied Sciences at Münchberg, May 1992.

41 Schäfer K, 'Die natürliche Fluoreszenz von Wolle', *Textilveredlung,* 1992, **27,** 38–43.

42 Schindler W and Drescher P, 'Fluoreszenzmarkierung von applizierten Siliconen zur Kontrolle ihrer Verteilung', *Melliand Textilberichte,* 1999, **80,** 67–68.

43 Hesse R and Pfeifer H, 'Fluoreszenzmikroskopie zur Erkennung von Fehlerursachen an Textilien', *Textilveredlung,* 1974, **9,** 82–87.

44 Nettelnstroth K, 'Mikroskopische Fehlererkennung an Textilien', *Textil Praxis International,* 1983, **38,** 572–574, 668–671.

45 Meyer U and Zürcher J, 'Charakterisierung von Baumwollveredlungsprodukten mit fluoreszierenden Verbindungen, 2. Teil: Zweifarbeneffekte mit Hilfe der Doppel-fluoreszenz', *Textilveredlung,* 1976, **11,** 325–329.

46 Meyer U, 'Selektive Markierung von Filzfreiausrüstungen auf Wolle mit fluoreszierenden Verbindungen', *Textilveredlung,* 1982, **17,** 440–446.

47 Weigmann H D, Steenken I, Moore R A F and Ruetsch S, 'Analysis of dye transport phenomena in Hercosett treated wool by microspectrophotometry', *Proceedings of the 7th International Wool Textile Research Conference,* volume **5**, 141–150, Tokyo, 1985.

48 Schäfer K and Gröger B, 'Fluoreszenzmikroskopische Untersuchungen zur Verteilung von Polymeren auf Wolle', *Schriftenreihe des Deutschen Wollforschungsinstitutes an der TH Aachen,* 1990, **105**, 173–184.

49 Schäfer K, Thomas H and Phan K H, 'Mikroskopische Untersuchungen an pflegeleicht-ausgerüsteter Wolle', *Schriftenreihe des Deutschen Wollforschungsinstitutes an der TH Aachen,* 1992, **109,** 613–631.

50 McCarthy B J and Greaves P H, 'Eigenfluoreszenz von Standard-Bioschädlingen bei Textilien', *Melliand Textilberichte,* 1990, **71,** 913–914.

51 Degruy I V and Carra J H, 'Structural aspects of the walls of cateye cotton', *Textile Research Journal*, 1977, **47,** 91–96.

52 Gutmann R and Herlinger H, Zürcher-Vogt J, 'Spinnpräparationen – Zusammenhänge zwischen Struktur und Wirksamkeit', *Chemiefasern/Textilindustrie*, 1992, **42/94,** 886–893.

53 Lewis D M and Smith S M, 'Reactive dyes and wool damage', *Proceedings of the 8th International Wool Textile Research Conference,* volume **4**, 177–186, Christchurch, New Zealand, 1990.

54 Lewis D M and Smith S M, 'The role of vinylsulphonyl reactive dyes in prevention of wool damage', *Journal of the Society of Dyers and Colourists,* 1991, **107,** 357–362.

55 Schindler W and Wegmann S, 'Kontrolle der Binderverteilung in dunklen Vliesstoffen', *International Textile Bulletin Vliesstoffe-technische Textilien,* 1998, **44**(4), 28–30.

56 Wortmann F J, 'Quantitative fiber mixture analysis by scanning electron microscopy. Part III: Round trial results on mohair/wool blends', *Textile Research Journal,* 1991, **61**, 371–374.

57 Mastura R (ed.), *Modern Textile Characterization Methods*, New York, Marcel Dekker, 1996.

58 Latzke P M and Hesse R, *Textile Fasern. Rasterelektronenmikroskopie der Chemie- und Naturfasern,* Frankfurt/Main, Deutscher Fachverlag, 1988.

59 Grieve M C, 'Fibers and their examination in forensic science', in *Forensic Science Progress,* Maehly A and Williams R L, (eds), volume **4**, Berlin, Springer-Verlag, 1990, 41–125.

60 Jacquemart J and Monrocq R, 'Fibrotome Institut Textile Francais', *Bulletin ITF,* no 120, September 1965.

61 Rohner P and Bruner J, 'Eine Dünnschliffmethode zur Herstellung von Querschnitten', *Textilveredlung,* 1983, **18,** 77–99.

62 Wagner E, 'Knopfmethode', *Mittex*, 1990, Number 12, 496–499.

63 Wagner E, Professionelle mikroskopische Querschnitte (Sandwich-Nassdünnschliff-Technik)', *Textilveredlung,* 1998, **33,** 85–90.

64 Producer Heraeus Kulzer GmbH, D-61273 Wehrheim, Germany.

65 Stahl E, *Thin-layer Chromatography, a laboratory handbook,* 2nd edn, New York, Springer/Academic Press, 1969.

66 Randerath K, *Thin-layer Chromatography,* New York, Verlag Chemie/Academic Press, 1966.

67 Kirchner J G, *Thin-layer Chromatography,* New York, Wiley-Intersience, 1967.

68 Nyderi S (ed.), *Planar Chromatogaphy – a retrospective view for the third millennum,* Budapest, Springer Scientific Publisher, 2001.

69 Fried B and Sherma J, *Thin-layer chromatography,* 4th edn, Chromatographic sciences series volume 81, New York, Marcel Dekker, 1999.

70 Rettie G H and Haynes C G, 'Thin-layer chromatography and its application to dyes', *Journal of the Society of Dyers and Colourists,* 1964, **80,** 629.

71 Anonymous, *Textilprüfung und Analysen,* SVF-Broschüre als Separatdruck aus dem SVF-Lehrgang für den Textilveredler, Basel, Schweizerische Vereinigung von Färbereifachleuten, 1975.

72 Schweppe H, 'Thin-layer chromatography', in *The Analytical Chemistry of Synthetic Dyes,* Venkataraman K (ed.), New York, John Wiley & Sons, 1977.

73 Küster B and Wahl U, 'Einfacher Nachweis von aromatischen Aminen als Spaltprodukte verbotener Azofarbstoffe', *Textilveredlung,* 1997, **32,** 121–124.

74 Löffel H, 'Die Untersuchung von Flecken auf Textilien im Bereich der Veredlungsprozesse', *Textilveredlung,* 1974, **9,** 75–82.

75 Weber-Kälin U, 'Textilchemische Schadensfallanalyse – Methoden und Praxisbeispiele', papers presented at the University of Applied Sciences at Münchberg, October 1991 and December 1997.

76 Kobayashi Y, 'Thin-layer chromatography of ε-caprolactam and its cyclic oligomers', *Journal Chromatography,* 1966, **24,** 447–450.

77 Lang B and Makart H, 'Polyester-Oligomere und ihre Bestimmung', *Melliand Textilberichte,* 1975, **56,** 647–651.

78 Furrer M., EMPA St. Gallen, Schweiz, personal communication.

79 York H, Funk W, Fischer W and Wimmer H, *Thin Layer Chromatography,* Volume 1a, Weinheim, VCH Verlag, 1990.

80 Armstrong D W and Stine G Y, 'Separation and quantitation of anionic, cationic and nonionic surfactants by TLC', *Journal Liquid Chromatography,* 1983, **6,** 23.

81 Bürger K, 'Dünnschichtchromatographische Methode zur Bestimmung der Molgewichtsverteilung und des Oxäthylierungsgrades von Polyäthylenoxidverbindungen', *Zeitschrift Analytische Chemie,* 1963, **196,** 259–268.

82 Bey K, 'Die dünnschichtchromatographische Analyse auf dem Gebiet der Tenside', *Fette Seifen Anstrichmittel,* 1965, **67,** 217–221.

83 Brüschweiler H, Sieber V and Weishaupt H, 'Dünnschichtchromatographische Analyse von anionaktiven und nichtionogenen Tensiden', *Tenside Detergents,* 1980, **17**, 3.

84 Günzler H and Gremlich H-U, *IR Spectroscopy. An introduction,* New York, Weinheim, Wiley-VCH, 2002.

85 Garton A, *Infrared Spectroscopy of Polymer Blends, Composites and Surfaces,* München, Carl Hanser Verlag, 1992.

86 Socrates G, *Infrared Characteristic Group Frequencies, Tables and Charts,* 2nd edn, Chichester, Wiley, 1997.

87 Kirkbride P and Tungol M, 'Infrared microscopy of fibres', in *Forensic Examination of Fibres,* Robertson J and Grieve M C, (eds), 2nd edn, London, Taylor & Francis, 1999, 179–222.

88 Schindler W, 'Textile Qualitäts-, Schadensfall- und Fremdmusteranalyse mit einfachen IR-Methoden, Teil 1: Transmission', *Melliand Textilberichte,* 2003, **84,** 764–767.

89 Schindler W, 'Textile Qualitäts-, Schadensfall- und Fremdmusteranalyse mit einfachen IR-Methoden, Teil 2: Gerichtete und diffuse Reflexion sowie ATR', *Melliand Textilberichte,* 2003, **84,** 990–993.

90 Schindler W, Müller G, Rupprecht M and Westphal C, 'Identifizierung von Vliesstoffbindern, insbesondere durch Infrarotmikroskopie', *Technische Textilien,* 1998, **41,** 205–207.

91 Hummel D O, *Atlas of Polymer and Plastics Analysis,* volume 1, 3rd edn, Weinheim, VCH, 1991.

92 Pouchert C J, *The Aldrich Library of Infrared Spectra,* Milwaukee Wisconsin, Aldrich Chemical Company Inc., 1981.

93 Pachler G R, Matlock F and Gremlich H-U, *Merck FT-IR Atlas,* Weinheim, VCH, 1988.

94 *Sadtler Databases for FT-IR, e.g. 'Fibers & Textile Chemicals' or 'Hummel/Sadtler Polymers',* Bio-Rad Laboratories Ltd, Hemel Hempstead, Herts HP2 7TF, England.

95 Ehrenstein G W, Riedel G and Traviel P, *Praxis der Thermischen Analyse von Kunststoffen,* München/Wien, Hanser-Verlag, 1998.

96 Turi E A, *Thermal Characterization of Polymeric Materials,* New York, Academic Press, 1997.

97 Hemminger W F and Cammenga H K, *Methoden der Thermischen Analyse,* Berlin, Springer-Verlag, 1989.

98 Hot bench (Heizbank), System Kofler, Cambridge Instruments, D-69226 Nussloch, Germany.

99 Wiesener E, 'Differential-thermoanalytische Untersuchungen an Polyäthylenterephthalat, Teil II: Ein endothermer Peak an der Fixiertemperatur', *Faserforschung und Textiltechnik,* 1968, **19** 301–303.

100 Lawton E L and Cates D M, 'Crystallization of polyethylene-terephthalate', *ACS Polymer Preprints,* 1968 **9** 851–859.

101 Heidemann G and Berndt H-J, 'Effektivtemperatur und Effektivspannung, zwei Meßgrößen zur absoluten Bestimmung des Fixierzustandes von Synthesefasern', *Melliand Textilberichte*, 1976, **57,** 485–488.

102 Jeziorny A, 'Mechanism of the appearance of the mobile peak on the thermograms of polyethyleneterephthalate fibres', *Acta Polymerica,* 1986, **37,** 237–240.

103 Fischer K, 'Die Glastemperatur. Orientierender Massstab für Polymer-Dispersionen,' *Textilveredlung,* 1984, **19,** 146–152.

104 Berndt H-J, 'Thermomechanische Analyse in der Textilprüfung – Methodik und Anwendung', *Textilpraxis International,* 1983, **38,** 1241–1245 and 1984, **39,** 46–50.

105 Bigler N, 'Die mikrokopische Untersuchung von Schadenfällen an Geweben und Gewirken mit Hilfe des Auflichts, Durchlichts und der Oberflächenabdruckmethode mit Gelatineplatten', *SVF-Fachorgan,* 1960, **15**(4), 251–259.

106 Mahall K, 'Untersuchung von Garnoberflächen im Abdruck', *Textilveredlung,* 1986, **21,** 342–348.

107 Atlas fabric streak analyzer, Atlas Electric Devices Company, Chicago, Illinois 60613 USA, or Atlas SFTS B.V., Mühlheim/Ruhr, Germany.

108 for example DIN 54278, Prüfung von Textilien – Auflagerungen und Begleitstoffe – Teil 1, Edition 1995–10: Bestimmung der in organischen Lösungsmitteln löslichen Substanzen; Teil 2, Edition 1978–02: Bestimmung des mit Salzsäure abziehbaren Anteils von ausgerüsteten Textilien.

109 Bors H, 'Zerstörungsfreie Materialkontrolle durch erzwungene Desorption', *Melliand Textilberichte,* 1997, **78,** 88.

110 Rieke I, 'Quantitative Faseranalyse mittels Morapex S Prüftechnik', *Melliand Textilberichte,* 1998, **79,** 605–606.

111 Eisenhut O, 'Zur Frage der Bestimmung des Schädigungswertes von Fasern, Garnen oder Geweben aus Zellulose und von Zellstoffen', *Melliand Textilberichte,* 1941 **22,** 424–426.

112 Hardt P *et al.*, 'Bestimmung des Durchschnittspolymerisationsgrades cellulosischer Fasermaterialien', *Melliand Textilberichte,* 1998, **79,** 640.

113 Schefer W, 'Faser- und Textilprüfung durch Viskosimetrie', *Textilveredlung,* 1969, **4**(8), 613–620.

114 Cybulska M, Goswani B C and MacAlister D III, 'Failure mechanism in staple yarns', *Textile Research Journal,* 2001, **71**, 1087–1094.

115 Plawat D, Shah P H and Plawat V, 'Objectionable faults in rotor spun cotton yarns: their identification, causes of generation and remedies', *41st Joint Technological Conference*, Resumé of Papers, 2000, Mumbai, Bombay Textile Research Association, 19–25.

116 Berndt H-J, 'Fehler in Geweben – Ursachen, Möglichkeiten der Reduzierung', *Textil Praxis International,* 1984, **39,** 238–241 and 331–336.

117 Iyer C, Mammel B and Schäch W, *Circular knitting; Rundstricken. Theorie und Praxis der Maschentechnik,* Bamberg, Meisenbach, 2000.

118 Bieser H, 'Fehlerarten und Fehlermöglichkeiten bei der Herstellung von Kettenwirkware', *Chemiefasern,* 1966, **16**, 554–559.

119 ISO 8499: 2003, *Knitted fabrics – Description of defects – Vocabulary.*

120 Venkataraman A and Walunj V E, 'Defects in knitted fabrics', *The Indian Textile Journal,* 1999, **110**, 122–126.

121 Weber R, 'Schäden an waschbaren Textilien – Ursachen und Verhütung', *Textilveredlung,* 1979, **14**, 129–137.

122 Koch P-A and Hefti H, *Textil-Rundschau,* 1956, **11,** 512–519, 645–655.

123 Evidence gathered at the Textile Chemical Laboratory of the University of Applied Sciences Hof, department Münchberg.

124 Sommer H, *Monatsschrift für Textilindustrie,* 1927, p. 158.

125 Available, for example, from Merck, Darmstadt, Germany.

126 Producer FESAGO, Chemische Fabrik Dr. Gossler GmbH, D-69207 Sandhausen, Germany.

127 Schliefer K and Heidemann G, 'Untersuchung zum Schädigungsmechanismus durch katalythaltige Verunreinigungen bei der Peroxidbleiche von Baumwolle', *Melliand Textilberichte,* 1989, **70,** 856–864 and 933–937.

128 Bechter D, Karagiozidis P, Herlinger H, Locke K and Bader E, 'Entfernung der Natronlauge aus cellulosischen Fasern', *Melliand Textilberichte,* 1991, **72,** 42–45.

129 Hermanutz F, Herlinger H and Bechter D, 'Quantitative Bestimmung des Mercerisiergrades. Teil 1: Methoden, die auf der gesteigerten Sorption basieren', *Textil Praxis International,* 1994, **49**, 495–499.

130 Thibodeaux D P and Price J B, 'Referenzmethode zur Bestimmung des Reifegrades von Baumwolle', *Melliand Textilberichte,* 1989, **70**, 243–246.

131 Xu B and Pourdeyhimi B, 'Evaluating maturity of cotton fibers using image analysis: Definition and algorithm', *Textile Research Journal,* 1994, **64,** 330–335.

132 Matic-Leigh R and Cauthen D A, 'Determining cotton fiber maturity by image analysis. Part 1: Direct measurement of cotton fiber characteristics', *Textile Research Journal,* 1994, **64,** 534–544.

133 Hermanutz F, *Methoden zur quantitativen Bestimmung des Mercerisiergrades von Baumwollgeweben/Methods for quantitative analysis of degree of mercerizing of cotton fabric*s, Dissertation, Universität Stuttgart, 1991.

134 Glosh S and Dilanni D, 'Estimating the degree of mercerization using near-infrared spectroscopy', *Journal of the Textile Institute,* 1994, **85**, 308–315.

135 Denter U, Bossmann A, Dugal S and Schollmeyer E, 'Anwendung des Rot/Grün-Tests zur Erkennung von Spannungsunterschieden bei Laugierprozessen', *Melliand Textilberichte,* 1984, **65,** 420.

136 Agster A, 'Die Einwirkung höherer Temperaturen auf natürliche und synthetische Faserstoffe', *Melliand Textilberichte,* 1956, **37**, 1338–1344.

137 Agster A, 'Zur Kenntnis des photochemischen Abbaus mattierter und nichtmattierter Zellulosefasern II', *Melliand Textilberichte,* 1955, **36**, 1–4.

138 Goynes W R, Bel-Berger P D, Blanchard E J, Ingber B F, Graves E E, Dastoor P and Von Hover T M 'Identification, qualification, and elimination of white speck defects on dyed cotton fabrics', *Textile Chemist and Colorist,* 1996, **28**(12), 25–29.

139 Peter U and Bowes Q, 'Quality variations in cotton and their effects on bleaching, dyeing and finishing – Qualitätsunterschiede in Baumwolle und deren Auswirkungen in der Veredlung', *Melliand Textilberichte,* 1989, **70,** 135–137.

140 Furter R, Frey M, 'Analyse des Spinnprozesses durch Messung von Zahl und Größe der Nissen', *Melliand Textilberichte,* 1991, **72,** 504–510.

141 Schneider T, Rettig D and Harig H, 'Reifegradprüfung an Baumwollfasern mittels rechnergestützter Bildanalyse', *Melliand Textilberichte,* 1997, **78,** 131–133.

142 Hadwich F, 'Der Reifegrad der Baumwolle', *Internationales Textil Bulletin Spinnerei,* 1975, **21**(1), 13–30.

143 Goldthwait C F, Smith H O and Barnett M P, *Textile World,* 1947, **97,** 105–108, 201, 202, 204, 206.

144 Koch P-A, 'Reifegradbestimmung an Baumwolle nach verschiedenen Prüfverfahren', *Zeitschrift ges. Textilindustrie,* 1970, **72,** 399.

145 Denter U, Bossmann A, Dugal S, Heidemann G and Schollmeyer E, 'Farbausfall des Rot/Grün-Tests auf Baumwollflocken unterschiedlichen Reifegrades in Abhängigkeit von der Vorbehandlung der Fasern', *Melliand Textilberichte,* 1986, **67,** 343–344.

146 Kornreich E, 'Ein Beitrag zur Untersuchung textiler Schäden', *Textil-Rundschau,* 1958, **13,** 458–464.

147 Rockstroh E *et al.*, *Prüfen von Textilien. Band II: Mikrountersuchungen,* 2. Aufl., Leipzig, VEB Fachbuchverlag, 1974.

148 Goebel I, Cognis/Henkel, personal communication, 1994.

149 Leube H, *Färben und Ausrüsten von Acetat und Triacetat und deren Mischungen mit anderen Fasern,* BASF-Ratgeber, Ludwigshafen, 1968.

150 Doehner H and Reumuth H, *Wollkunde,* Berlin, Paul-Parey-Verlag, 1964.

151 Herzog A, 'Nachweis von Wollschädigungen mit Indigokarmin', *Melliand Textilberichte,* 1931, **12**, 768–769.

152 Still available, for example Merck, Darmstadt, Germany, Art.Nr. 105233.

153 Sigma-Aldrich Chemie GmbH, D-82024 Taufkirchen, 4-Benzobenzolsulfonsäure = Fluka Nr. 33492.

154 Krais P, Markert H and Viertel O, *Forschungshefte der Deutschen Forschungsinstitute Dresden,* 1933 and 1935.

155 Zahn H, 'Schädigung beim Karbonisieren und Nachweismethoden (I)', *Textil Praxis International*, 1959,**14**, 928–930.

156 IWTO is the International Wool Textile Organisation, IWTO Regulations available from The Woolmark Company, West Yorkshire, England.

157 Zahn H, Wulfhorst B and Külter H, Faserstoff-Tabellen nach P-A Koch: Wolle (Schafwolle) – Feine Tierhaare, *Chemiefasern/Textilindustrie,* 1991, **41/93,** 521–553.

158 Schäfer K, 'Determination of the amino acid tryptophan in protein fibres', *Journal of the Society of Dyers and Colourists,* 1997, **113**, 275–280.

159 Schäfer K, Föhles J and Höcker H, 'Lichtschädigung bei Wolle und anderen Proteinfasern', *Melliand Textilberichte,* 1993, **74,** 225–231.

160 Sakli F and Schutz R A, 'Qualitätskontrolle der Wolle durch Löslichkeitsversuche', *Melliand Textilberichte,* 1988, **69**, 366–368.

161 Schefer W, 'Schädigung von Wolle durch Veredlungsoperationen, insbesondere beim Färben', *Melliand Textilberichte,* 1982, **63**, 368–370.

162 Schöberl A, 'Erfahrungen und Probleme bei der Bestimmung von Cystin in Wollen und Haaren', *Textil Praxis International,* 1959, **14**, 701–708.

163 Schönberger W, 'Erfahrungen mit der Cystinanalyse bei der Bearbeitung von Reklamationen', *Textil Praxis International,* 1959, **14**, 600–606.

164 Sanger F, *Biochem. Journal,* 1949, **45**, 563 (quoted from Chwala A, Anger V, *Handbuch der Textilhilfsmittel*, Weinheim New York, Verlag Chemie, 1977).

165 Mahall K and Goebel I, 'Fortschritte auf dem Gebiet des Entbastens der Seide', *Textilveredlung,* 1988, **23**, 8–16.

166 Anonymous, 'Accidents sur soie', *Revue de l'Entretien des Textiles et du Nettoyage',* 1996, **20**, 14–21.

167 Kornreich E, *J. Text. Inst.,* 1950, **41**, 321–328 (quoted from Hoffmann L, *Spinnerei und Weberei,* 6/1962, 520–524).

168 Jutao-Luo and Jihong-Cao, 'Low temperature dyeing of real silk fabrics with liquid sulphur dyes', *Journal of the Society of Dyers and Colourists,* 1997, **113**, 67–69.

169 Svilokos B, 'Controlli su seta', *Tinctoria,* 1988, **85**, 53–58.

170 Bianchi A and Massafra M R, 'Fehler in Naturseide-Produkten', *Melliand Textilberichte,* 1986, **67**, 706–709.

171 Mahall K, 'Silk and its treatment', *Textile Asia,* 1985, **16**, 95–101.

172 Anonymous, 'In laboratorio – difetti su seta', *La Seta,* 1984, 28–30.

173 Svilokos B and Previato I, 'Nuovi sistemi di sgommatura: Possibili cause della degradazione della fibroina da Bombix Mori e metodi di controllo', *La Seta,* 1983, 8–16.

174 Shenai V A and Singhi A B, 'Photochemical degradation of dyed tasar', *The Indian Textile Journal,* 1981, **91**, 111–117.

175 Knott J, Freddi G and Belly M, 'Analytische Untersuchungen zum Entbasten von Seide', *Melliand Textilberichte,* 1983, **64**, 481–483.

176 Flensberg H and Hammers I, 'Naturseide und ihre Veredlung', paper presented at the *Naturseide-Symposium*, Haus der Technik, Essen, Germany, November 1987.

177 Gavet L, Ambroise G and Giorgio A, 'Organic weighting of silk by grafting', *Technical Report ITF,* Lyon, 1983.

178 Schindler W and Wiesel U, 'Nachweis der Methacrylamid-Erschwerung von Seide', *Melliand Textilberichte,* 1999, **80**, 546–548.

179 Schwertassek K, 'Methoden zur Feststellung des Fixiergrades an Synthesefasern. Ihre Bedeutung für Praxis und Forschung', *Textilindustrie,* 1964, **66**, 918–923.

180 Buchanan D R and Hardegree G L, 'Thermal stress analysis of textile yarns', *Textile Research Journal,* 1977, **47**, 732–740.

181 Hearle J W S, 'Fibre fracture and textile durability – part 2', *Textiles Magazine,* 1999, **28**, 15–21.

182 Bigler N, 'Ein Beitrag zur Erkennung von Fehlern in Flachzwirngarnen', *Textilveredlung,* 1966, **1**, 152–156.

183 Nanal S Y, 'Problems occuring in manufacture of polyester staple fibre', *Journal of the Textile Association,* 2001, **62**, 49–52.

184 Topf W, 'Fehler bei der Verarbeitung von Chemiefasern', *Textil Praxis International,* 1983, **38**, 641–644.

185 Zimmermann R, DyStar, personal communication, 2003.

186 Schaich B, *Bestimmung der Fixierunterschiede von Polyestergewebe, vorzugsweise durch Polarisationsmikroskopie*', Undergraduate Thesis, University of Applied Sciences at Münchberg, 1993.

187 Berndt H-J, Heidemann G, 'Fehlerursachen und Erkennungsmethoden von Farbstreifigkeit in Polyester-Material', *Deutscher Färber-Kalender,* 1972, **76**, 408–479.

188 Wiley R E, 'Setting up a density gradient laboratory', *Plastics Technology,* March 1962, and *Österreichische Chemiker-Zeitung,* 1965, **66**, 65–72.

189 Gacén J, Maillo J and Barón A, 'Einfluss des Texturierprozesses auf die Feinstruktur von thermofixiertem Polyester', *Melliand Textilberichte,* 1989, **70**, 12–14.

190 Gacén J, Maillo J and Naik A, 'Jodsorption und Festigkeitsparameter von LOY-, MOY-, POY- und FOY-Polyestergarnen', *Melliand Textilberichte,* 1988, **69**, 867–870.

191 Richter K, 'Beitrag zu chemischen Charakterisierung der Polyacrylnitril- und Polyesterfasern', *Deutsche Textiltechnik,* 1961, **11**, 316–320.

192 Bobeth W, Möglichkeiten der Fixiergradprüfung an synthetischen Faserstoffen mit Hilfe mikroskopischer Methoden', *Textilindustrie,* 1965, **67**, 67–73 and older publications, quoted here.

193 Schwertassek K, 'Zur Aufklärung färberischer Ungleichmäßigkeiten an texturierten Polyestergarnen', *Textil Praxis International,* 1974, **29**, 96–100.

194 Küppers H, 'Textiluntersuchung – nicht aufwendig', *Textilveredlung,* 11974, **9**, 67–71.

195 SNV 95591, Prüfung auf Faserveränderung und Faserschädigung: Bestimmung der Viskositätszahl von Polyesterfasern in m-Kresol, *Textil-Rundschau,* 1964, **19**, 331–334.

196 Tetzlaff G, Dahmen M and Wulfhorst B, 'Faserstoff-Tabellen nach Koch P-A: Polyesterfasern', *Chemiefasern/Textilindustrie,* 1993, **43/95**, 508–522.

197 Denter U, Elgert K-F and Heidemann G, 'Farbtest zur Charakterisierung abgeschälter Polyesterflächen', *Melliand Textilberichte,* 1987, **68**, 848.

198 Busert F, 'Anfärbemethoden zur Früherkennung des Barée-Effektes an Polyesterfasern', *Melliand Textilberichte,* 1976, **57**, 229–234.

199 Weber R, 'Lichtmikroskopische und elektronenmikroskopische Untersuchungen an lichtgeschädigten Polyesterfasern', *Textilveredlung,* 1970, **5**, 703–708.

200 Valk G, Kehren M-L and Daamen I, 'Über die Photooxidation von Polyäthylenglykolterephthalat-Fasern', *Angewandte Makromolekulare Chemie,* 1970, **13**, 97–107.

201 Day M and Wiles D M, 'Photochemical Degradation of Poly(ethylene terephthalate). III. Determination of Decomposition Products and Reaction Mechanism', *Journal of Applied Polymer Science,* 1972, **16**, 203–215.

202 Anonymous (probably Höhn W), *Oligomere – Phänomen, Analyse und Minimierung von PES-Olgomeren*, Firmenschrift Dr. Th. Böhme, Geretsried, 1997.

203 Bubser W, Modlich H, 'Erkennung und Unterscheidung von Schäden an Polyamidfasern (Perlon und Nylon)', *Textil Praxis International,* 1959, **14**, 1041–1043 and 1152–1158.

204 Modlich H, 'Beurteilung des Fixiergrades an Perlon durch Schnittendenquellung', *Melliand Textilberichte,* 1959, **40**, 906–911.

205 Gosh S and Rodgers J E, 'Schnelle Identifizierung von hitzefixierten Teppichgarnen durch Reflexionsanalyse im nahen Infrarotgebiet', *Melliand Textilberichte,* 1988, **69**, 361–363.

206 Kratzsch H and Hendrix H, 'Zur Unterscheidung von Licht- und Säureschäden bei Polyamidfasern', *Melliand Textilberichte,* 1964, **45**, 1129–1133.

207 Reinert G, 'Zur Photostabilität der Polyamidfaser', *Melliand Textilberichte,* 1988, **69**, 58–64.

208 Bever M, Breiner U, Conzelmann G and von Bernstorff B-S, 'Protection of polyamide against light', *Chemical Fibers International,* 2000, **50**, 176–178.

209 Leumer G, Böhme S and Rossbach V, 'Aminoendgruppenanalyse aliphatischer und teilaromatischer Polyamide mit 1-Fluor-2,4-dinitrobenzol in Benzylalkohol', *Melliand Textilberichte,* 1991, **72**, 1026–1031.

210 SNV 95590, Prüfung auf Faserveränderung und Faserschädigung: Bestimmung der

Viskositätszahl von Polyamidfasern in m-Kresol, *Textil-Rundschau,* 1964, **19**, 217–220.

211 Zaremba S, Steffens M, Wulfhorst B and Hirt P, 'Faserstoff-Tabellen nach Koch P-A: Polyamidfasern', *Melliand Textilberichte,* 1997, **78**, 771–794.

212 Schwertassek K, *Faserforschung und Textiltechnik,* 1958, **9**, 321 and 1954, **5**, 493.

213 Gries T, Rixe C, Steffens M and Cremer C, 'Faserstofftabellen nach P-A Koch: Polyacrylfasern', *Melliand Textilberichte,* 2002, **83**, 795–816.

214 Sarhadjieva V, Nankova Z and Dimov K, 'Influence de l'étirage et du traitement thermique sur les propriétés des fibres acryliques', *Ann. Sci. Textiles Belges,* 1975, 164–183.

215 Gacén J and Arias J M, 'Die kritische Auflösezeit für Acrylfasergarne – The critical solution time of acrylic fibre yarns', *Melliand Textilberichte,* 1980, **61**, 533–536.

216 Rossbach V and Karunaratna N, 'Beständigkeitsprüfung technischer Textilien mit der Methode der kritischen Lösezeit', *Melliand Textilberichte,* 1985, **66**, 223–226.

217 Heinkel H, 'Einfache PAC-Faser-Identifizierung für den Praktiker', *Textilveredlung,* 1977, **12**, 403.

218 Drechsel B, Hoffmann F and Ottner S, 'Rechnergestützte Optimierung diskontinuierlicher Färbeverfahren – Weg zur Kostensenkung und fehlerfreien Produktion'; *Melliand Textilberichte,* 1998, **79**, 328–332.

219 Drechsel B, Hoffmann F and Ottner S, 'Computer supported optimisation of discontinuous dyeing processes – cost reduction and fault-free production', *Melliand International,* 1998, **4**, 114–117.

220 Beckmann W, 'The sytematics of dyeing synthetic fibres in exhaust dyeing', DyStar brochure TD WB 8015 E, 1996, p. 56 and 'Die Sytematik des Färbens von Synthesefasern nach dem Ausziehverfahren', Broschüre Sp 627, D4/800 6569, S. 57, Bayer AG, 1994.

221 Neal B L, 'Repairing off-quality acrylic dyeing', *American Dyestuff Reporter,* 1980, **69**, 26–27.

222 Anonymous, 'Las causas de accidentes tipicos en la limpieza en secco', *Rev. Tec. Tintoreria y Lavand.,* 1987, 47–51 and 1985, 53–54.

223 CTTN, 'L'entretien des articles en fourrure artificielle ou synthetique', *Entretien des textiles,* 1976, **67**, 17–24.

224 Koch P-A, Faserstofftabelle Polyacrylnitrilfasern und Modacrylfasern, *Chemiefasern/ Textil-Industrie,* 1977, **27/79**, 513–524.

225 Anonymous, 'Dow XLA-Faser jetzt Lastol', *Melliand Textilberichte,* 2003, **84**, 242.

226 Fabricius M, Gries T and Wulfhorst B, Faserstofftabellen nach Koch P-A: Elastanfasern, 2nd edn, *Melliand Textilberichte,* 1995, **76**, 980–990.

227 Gähr F and Lehr T, 'Bedeutung thermischer und hydrothermischer Prozesse als Ursache von Elastanschädigungen', *Melliand Textilberichte,* 2001, **82**, 722–725.

228 Gähr F and Lehr T, 'Ursachen von Elastanschädigungen bei der Veredlung von Maschenwaren', *Maschen-Insustrie,* 2002, **52**, 38–41.

229 Küster B and Herlinger H, 'Untersuchungen zum photochemischen Abbau von Elastomerfasern', *Textil Praxis International,* 1981, **36**, 15–21.

230 Hueber H, 'Praktische Aspekte bei der Veredlung von elastischen Textilien', *Melliand Textilberichte,* 1998, **79**, 243–246.

231 Naroska D, 'Chancen und Risiken beim Veredeln elastischer Textilien', *Melliand Textilberichte,* 1999, **80**, 611–615.

232 Freiberg H, 'Indirekte Gasheizung für Spannrahmen und Hotflues', *Melliand Textilbderichte,* 2002, **83**, 330–334.

233 Falkai B v, *Synthesefasern,* Weinheim, Verlag Chemie, 1981.

234 Schmenk B, Miez-Meyer R, Steffens M, Wulfhorst B and Gleixner G, 'Fiber tables

according to Koch P-A: Polypropylene fiber table', 2nd issue, *Chemical Fibers International,* 2000, **50**, 233–253.

235 Anonymous, 'Dow XLA-Faser jetzt Lastol', *Melliand Textilberichte,* 2003, **84**, and references therein: *Chemical Fibers International,* 2002, **52**, 373 and *Melliand International,* 2003, **9**, 4.

236 Wang Y, Feng X and Sivakumar M, 'Improving sewability of PP knitted fabric', *The Indian Textile Journal,* 1998, **109**, 86–88.

237 Qian C and Chu C, 'Fatigue properties of the two composite geotextiles', *Journal of Dong Hua University,* English edition, 2002, **19**, 53–55.

238 Chidambaram A, Davis H and Batra S K, 'Strength loss in thermally bonded polypropylene fibers', *Joint INDA-TAPPI Conference, INTC 2000, International Non-wovens Technical Conference,* Book of Papers, Dallas USA, 2000, 19.0–19.23.

239 Wulfhorst B and Meier K, 'Faserstofftabellen nach Koch, P-A: Polypropylenfasern', 1st edn, *Chemiefasern/Textilindustrie,* 1989, **39/91**, 1083–1090.

240 Ripke C, 'Polypropylen-Fasern und ihre Pigmentierung', *Chemiefasern/Textilindustrie,* 1980, **30/82**, 30–35 and 110–114.

241 Martin E, 'Lichtbeständigkeit der Faserstoffe', *Textilveredlung,* 1983, **18**, 222–225.

242 Pezelj E, Cunko R and Andrassy M, 'The influence of repeated maintenance treatments on chemical and thermal properties of polypropylene fibers', *78th World Conference of the Textile Institute, 5th Textile Symposium of SEVE and SEPVE*, volume **III**, 395–400, Thessaloniki, Greece, 1997.

243 Ulmann E, 'Mikroskopische Untersuchungen an Rissenden von Textilfasern', *Textilveredlung,* 1982, **17**, 114–120.

244 Cunko R and Pezelj E, 'The influence of pollutants on weathering of polypropylene fibers in natural environment', *30th International Symposium on Novelties in Textiles,* 99–102, University of Ljubljana, Slovakia, 1996.

245 Dugal S and Schollmeyer E, 'Systematisierung der Analytik von Schlichtemitteln auf Geweben aus Cellulosefasern und deren Mischungen mit Synthesefasern', *Textil Praxis International,* 1984, **39**, 252–254.

246 Hemmpel W-H, 'Zum Problem der Lagervergilbung unverpackter, freihängender Textilien', *Textil Praxis International,* 1983, **38**, 261–264 and 354–355.

247 Diener H, *Fleckentfernung – aber richtig,* 10. Aufl., Leipzig, Fachbuchverlag, 1980.

248 Goebel I, 'Streifenbildung – Identifizierung häufig auftretender Fehler in Geweben und Wirkwaren', *Textilveredlung,* 1993, **28**, 389–394.

249 Nopitsch M, 'Beitrag zum Nachweis von Schimmel auf Baumwolle und von Wollschädigungen im allgemeinen', *Melliand Textilberichte,* 1933, **14**, 139–142.

250 Nopitsch M, *Textile Untersuchungen,* Stuttgart, Kohlhammer, 1951.

251 Heuse O and Adolf F-P, 'Non destructive identification of textile fibers by interference microscopy', *Journal Forensic Science Society,* 1982, **22**, 103.

252 Biermann T W and Grieve M, 'Die Zukunft der forensischen Faseranalyse', *Kriminalistik,* 2001, **55**, 337–340.

253 Grieve M C, 'Back to the future – 40 years of fibre examinations in forensic science', *Science & Justice,* 2000, **40**(2), 93–99.

254 Grieve M C, 'Fibers and forensic science – new ideas, developments, and techniques', *Forensic Science Review,* 1994, **6** (1), 60–79.

255 Gerbig M, 'EMPA News – TESS – Textiles Experten-System für Schadenfälle', *Textilveredlung,* 1993, **28**, 121.

256 Gerbig M and Hufenus R, 'TESS – Textiles Experten-System für Schadenfälle', *Textilveredlung,* 1993, **28**, 365–369.

257 Hufenus R and Gehring S, 'TESS – Wie man aus Schaden klug wird', *Internationales Textil Bulletin Garn und Flächenherstellung,* 1997, **43**(1), 50–55.
258 Gehring S and Hufenus R, 'Expertensystem für Schadenfälle', *Melliand Textilberichte,* 1998, **79**, 77–79.