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Aftertreatment of Anionic Dyes on Nylon Fibres
II—Effect of Postsetting on Dyed and Backtanned Nylon

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The wet fastness of dyed unbacktanned nylon fibres decreases slightly during dry-heat setting under moderately severe conditions. This is attributed mainly to oxidative degradation of the fibre, which also results in considerable yellowing and loss in strength. The wet fastness and tensile strength decrease slowly during prolonged steam setting, but several hours are required to produce a similar decrease to that produced by treatment for a few minutes in hot air. Yellowing of the fibre during steam setting is very slight, even on prolonged treatment. The rapid decrease in the wet fastness of backtanned nylon during setting occurs mainly in the early stages of treatment and the fastness decreases ultimately to that of the untanned and postset fibre. The improvement in wet fastness on backtanning is less on dyed nylon 6 than on nylon 6.6, because less of the agent is taken up by nylon 6. However, the wet fastness of aftertreated nylon 6 decreases more rapidly during setting because this fibre is more prone to thermal degradation. The most important causes of the loss in wet fastness of backtanned dyeings on nylon fibres are (*a*) thermal oxidation of the backtanning agent, (*b*) thermal and hydrolytic attack of the nylon and (*c*) catalysis of degradation of the nylon by the backtanning agent or its decomposition products.

Introduction

A nylon filament is a semicrystalline solid in which the regions of higher order are composed of groups of parallel segments of neighbouring chain molecules held together by hydrogen-bonding or dipolar forces between the amide groups and weak hydrophobic interaction between alkylene segments. The ordered regions are spherulitic and are formed during cooling of the polymer melt in the course of extrusion and formation of the filament. The spherulites are embedded in an amorphous matrix of randomly disposed polymer segments that are capable of some degree of rotatory or flexing movement accompanied by breaking and re-forming of interchain bonding forces. Regions of intermediate degrees of order exist around the fringes of the spherulites (*1*) and in those parts of the amorphous matrix that enable neighbouring segments to be aligned partially.

The internal stresses introduced in the filament by the tensions exerted during cold drawing increase with the proportion of crystalline and semi-ordered material present and the orientation of the ordered regions in the axial direction. These changes are accompanied by the formation of voids (*2*) and manifest as a slight increase in overall density (*3*) and a decrease in moisture regain (*4*). Moisture is sorbed by hydrogen bonding to the amide groups in the amorphous regions, but the amide groups within the crystalline regions are inaccessible to water molecules (*5*). The ingress of regain moisture, however, loosens the regions of intermediate order on the fringes of the spherulites and causes swelling. Sorption of water molecules within the amorphous matrix facilitates movement of the polymer segments on heating, permitting structural rearrangement to a state of greater stability (*6*).

The presence of folds in the molecular chains which pass through the crystalline and semi-ordered regions of the drawn yarn is responsible for strains and discontinuities of lattice order near the chain fold. During setting re-folding is believed to occur to improve the overall lattice order. This results in the voids surrounding the folds and chain ends tending to coalesce and form larger voids, so that the remainder of the neighbouring polymer segments adopt an improved alignment, and the degree of order of that part of the structure is increased. Nuclear magnetic resonance spectroscopy has given some insight into these rearrangements. The change in the long-period intensity assigned to chain folding is a measure of the fluid-like mobility of the structure. Re-folding is particularly favoured under conditions of steam setting, especially when the yarn is in a relaxed condition (*7*).

Irreversible dimensional changes occur during heat-setting processes or treatment of drawn filaments with swelling agents (*8*). Phenolic solvents readily form hydrogen bonds with amide groups and permit molecular rearrangements of chain segments (*9*), but the additional hydrophobic interaction between such swelling agents and the nonpolar segments of the polymer allow more extensive disorganisation of the ordered regions, leading ultimately to weakening and dissolution of the nylon. Natural polyphenols such as the hydrolysable tannins have considerable substantivity for nylon because of the many opportunities for hydrogen bonding between the phenolic groups and the amide sites. Simpler phenols of the gallic acid type are invariably present in the hydrolysable tannins and these can probably swell the nylon sufficiently to facilitate access of the larger polyphenol molecules.

The improvement in the wet fastness of anionic dyes on nylon resulting from aftertreatment with natural tannins is apparently attributable mainly to modification of the substrate by the tannin, which lowers the rate of diffusion of the dye through the amorphous matrix (*10*). The polyfunctional character of the tannin molecule enables it to form an effective bridge between neighbouring polymer segments. This reticulation of the flexible nylon segments causes some embrittlement of the polymer and is accompanied by significant losses in flexibility, tenacity and extensibility. Tartar emetic (potassium antimonyl tartrate) improves the effectiveness of backtanning by forming a less soluble complex with tannic acid which is more resistant to alkaline oxidation and removal on washing.

The improvement in the wet fastness of anionic dyes on nylon caused by aftertreatment with syntans of the sulphurised

phenol type, e.g. Taninol WR (ICI), is apparently attributable to (*a*) modification of the surface layers of the substrate to lower the rates of diffusion of the dye out of dyed nylon and into adjacent undyed fibres and (*b*) complex formation between the dye and the agent in solution to minimise staining of the undyed fibres. The relative importance of contributions from (*a*) and (*b*) will depend upon the relation between dye structure and stability of the dye–agent complex. Taninol WR has a significant effect on the physical properties of nylon, but the degree of embrittlement of the nylon by the syntan is considerably less than that caused by the natural tannin. This substantiates other evidence that the natural tannins penetrate the substrate deeply and considerably modify the internal structure of the fibre, whereas the syntan modifies only the surface regions of the filaments.

Heat-setting treatments are essential to control the behaviour of nylon materials during processing and subsequent use. Setting before dyeing (presetting) is useful to minimise creasing during scouring or dyeing in rope form. Setting after dyeing (postsetting) is usually necessary to improve the handle, dimensional stability and crease resistance of the finished fabric, but unfortunately postsetting seriously impairs the wet fastness of backtanned anionic dyeings.

The most important method of imparting durable set to a nylon fabric is by means of dry heat on a pin stenter; typical temperatures of treatment are 170–190°C for nylon 6 or 200–220°C for nylon 6.6. Despite the incorporation of antioxidants in nylon fibres during manufacture, they are prone to oxidative attack at temperatures approaching their melting point. Oxidation can be minimised by using coal-gas instead of air as the heating medium, but this method is not very useful because of the unfavourable effects of the products of combustion of this gas on the dyes used. The best method of preventing oxidation during dry-heat setting is to use an inert gas, such as nitrogen, but this makes the equipment much more expensive to install and operate.

Infrared heating is an alternative method of continuous setting on a pin stenter. Although the surface temperature of the infrared tubes is 350–400°C, discoloration of the fabric is less than in hot-air setting because of the relatively slow movement of air close to the fabric in the infrared zone and the existence of automatic devices to move the heaters away if the fabric is stopped. The setting conditions must be controlled very carefully because the fabric is exposed only briefly to the heat treatment, the regain moisture evaporates quickly and the fabric temperature rises quickly; there is no dwell-period at the maximum temperature as there is in most other methods of setting.

Nylon fabrics can also be set continuously by contact heat in a calendar nip, but this may give an undesirable stiffening of the fabric and there is little control of the width. Treatment in hot water (hydrosetting), organic solvents or aqueous solutions of swelling agents can be used to set fabrics, and unset fabrics usually acquire satisfactory dimensional stability by scouring and dyeing in open width.

The most important batchwise method of heat setting, however, is the application of high-pressure steam at 120–140°C (15–35 lb/in^2). Steam setting produces a fabric with a soft, full handle and good crease resistance, but the fabric width is not controlled and the yarns shrink during steaming to an extent determined by the heat treatments and tensions to which they have been exposed before setting. The presence of steam rather than hot air near the fabric affords protection from oxidation and provides a reservoir of molecules of water which swell the polymer structure and enable setting to occur at a much lower temperature than that necessary for dry-heat setting.

Forward and Palmer have compared the effectiveness of different kinds of setting treatment by measuring the irreversible changes in dimension of relaxed drawn nylon 6.6 yarn during setting (*9*). A contraction of 5% was observed during dry-heat treatment at 115°C and on immersion in water at 25°C. Similarly, a contraction of 12% could be obtained by dry heat at 190°C, by steaming at 25 lb/in^2 or by treatment with 2% aqueous phenol solution at 25°C. Although setting treatments carried out on relaxed yarns under these conditions may be regarded as approximately equivalent, they cannot be compared with the setting of yarns and fabrics under tension. The external stresses on a filament held under tension help to preserve the degree of crystallinity and orientation and restrict the mobility of the polymer segments in the amorphous regions.

DRY-HEAT SETTING

Accurate and reproducible control of time, temperature and fabric condition during setting is more important in dry-heat treatment than in steam setting. There is a limit to the severity of treatment that can be given and to the degree of set that can be imparted because the onset of thermal degradation is accompanied by yellowing of the nylon. It is advisable to cool the set fabric before batching because considerable heat may be retained in the roll of fabric and result in differences in dimensional stability, dyeability, yellowing and degradation between different batches or from inside to outside of the same batch.

During dry-heat setting the molecular chains in the nylon take up configurations different from those adopted when water is present to swell the regions of intermediate order surrounding the crystalline material. Peters and White consider that undrawn nylon 6.6 contains approximately 30% of crystalline regions orientated randomly with respect to the fibre axis and only 5% of highly disordered polymer, the remainder having some degree of ordered or semi-crystalline character (*1*). Cold drawing of the filaments increases the orientation of the ordered regions, but the internal stresses result in a loss in crystallinity by disorganisation of fringes of the crystalline material. Dry-heat setting temporarily increases the mobility of the polymer segments. At about 200°C the segments in the amorphous regions become mobile and at 240–250°C the partially ordered regions are sufficiently affected for new crystalline material to be formed at the expense of the semi-crystalline portion. This heat-induced crystallisation produces internal stresses, which lead to some disorientation of the existing structure.

The structural changes occurring in drawn nylon 6 filaments during setting have been studied by Rau and Schwair (*11*). Investigation by X-ray diffraction showed that the amount of monoclinic α-structure of the crystalline portion of the polymer increases by 20% and the proportion of amorphous material decreases correspondingly during the dry-heat setting of polycaprolactam at about 190°C. In tensionless setting, the X-ray diffraction patterns reveal only a slight loss in orientation of the crystallites, but measurement of the velocity of sound by pulse propagation through the filaments demonstrates that the orientation of the less ordered regions decreases considerably. These changes are prevented if the filament is held under tension during setting.

The effects of heat setting on the dyeability of nylon 6 and nylon 6.6 fibres have been studied in detail (*12–15*). Although the dyeing properties of anionic dyes are influenced much more than those of disperse dyes, the relation with setting temperature is broadly similar for all classes of dyes on both types of fibre. Dry-heat setting of nylon 6.6 at up to 220–230°C reduces the rate of dyeing and equilibrium uptake of practically all dyes. Heat treatment at temperatures closer to the melting point of the fibre produces so much degradation of the polymer that the dyeability of the untreated fibre is exceeded. The curve of rate of dyeing against setting temperature therefore shows a minimum at 190–210°C for nylon 6.6, the temperature of minimum dyeability increasing as the exposure time decreases. Application of tension during setting lowers the dyeability of the nylon.

Polycaprolactam responds similarly to poly(hexamethylene adipamide) with respect to the influence of setting on dyeability, but the temperatures of maximum influence and of zero influence are 20–30 degC lower.

STEAM SETTING

Steam-set fabrics have an attractive, full handle and excellent dimensional stability, but it is difficult to maintain a constant finished width because of weftway shrinkage during steaming. Peters and White (*1*) found that the amine end-group content of nylon 6.6 was practically unchanged after steaming for 30 min in superheated steam at 25 lb/in² and 130–205°C. There was no evidence of hydrolysis or degradation of the fibre during setting in saturated or superheated steam. The presence of residual air in the steam, however, can lower the effective temperature of setting and cause oxidation.

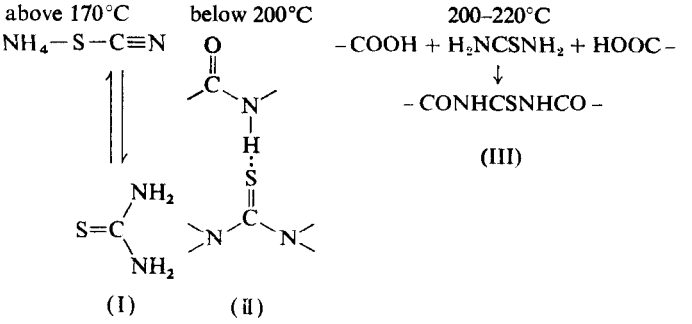
Moisture present in the nylon during steam setting loosens the partially crystalline regions by swelling, but the heating increases the amount of crystalline material at the expense of the semi-crystalline regions. At 130–135°C in saturated steam the amount of crystalline monoclinic α-structure in nylon 6 increases by about 30%, with a corresponding decrease in the proportion of the mesomorphic hexagonal γ-structure. Apart from this marked increase in the amount of α-crystalline material, the degree of order of the α-structure is increased and the ideal α-structural configuration is practically achieved in parts of the polycaprolactam filament (*11*). Superheated steam reverses this trend to some extent and filaments set in superheated steam are similar to those set by dry heat. Steam setting of nylon fabrics increases the rate of dyeing, the effect increasing gradually with setting temperature in the range 100–150°C, but, in general, the steaming has no influence on the equilibrium uptake of dyes. If the fabric is wound under excessive tension before steaming, its dyeability is lower than that of fabric set under tensionless conditions.

THERMAL DEGRADATION AND YELLOWING

The mechanisms of thermal degradation and photodegradation of nylon fibres are broadly similar in that they include free-radical chain reactions in which the methylene groups adjacent to carbonyl groups are attacked by peroxy radicals or activated oxygen, homolytic fission of weaker bonds in the structure and, probably, hydrolysis of amide groups and decomposition products by water molecules provided by steam or regain moisture. Agster found that heating in saturated steam with some air present caused more rapid decomposition than dry-heat setting at higher temperatures, because the mixture of air and steam favours the formation of hydrogen peroxide (*16*).

The relation between the decrease in degree of polymerisation of nylon 6.6 by decomposition of amide groups and the loss in tensile strength during the heat treatment of the fibre was investigated by d'Albignac (*17*). He showed that thiourea minimises yellowing and degradation and improves the fixation of 1:2 metal-complex disperse dyes in pad–thermofix dyeing at 210°C. Urea is not as effective as thiourea. Although *N*-methylthiourea is as effective as thiourea below 200°C, thiourea is much better in the range 200–230°C. The decomposition reactions overcome the effect of thiourea above 230°C, at which temperature the extent of decomposition is similar to that observed at 200°C in the absence of thiourea.

When thiourea is heated above 170°C a reversible transformation to ammonium thiocyanate takes place (I), the mixture containing about 25% of thiourea at equilibrium. Pure ammonium thiocyanate is greatly inferior to thiourea as a protective agent for the nylon. Thiourea and its monomethyl derivative are believed to form hydrogen bonds through the thioketone group and protect the amide group (II) from hydrolytic attack below 200°C. This effect is assumed to be reinforced for thiourea by



reaction with carboxyl end-groups (III), as the formation of αα′-diketothioureas from thioureas and simple carboxylic acids at 200–210°C is well known (*18*).

The importance of oxidation in the photodegradation of nylon was demonstrated by Egerton, who found negligible decomposition on irradiating nylon in an inert atmosphere (*19*). Many dyes accelerate the degradation by absorbing light energy and transferring this energy to oxygen in the surrounding atmosphere; the activated oxygen reacts with water present to form hydrogen peroxide. Nylon is susceptible to direct attack by the activated oxygen because the marked degradation occurring on exposure in dry air does not increase significantly on increasing the humidity. Some dyes exert a protective effect by absorbing the ultraviolet radiation below 330 nm which induces homolytic fission of amide bonds in the polymer.

Although the oxidation and depolymerisation during exposure of nylon to light and heat are similar in mechanism, and Bubser found that the characteristics of polycaprolactam degraded by either agency were almost identical, the rates of loss of the original properties of the polymer are not identical (*20*). In the initial stages of dry-heat treatment, losses in tensile strength of 10–15% may occur simply as a result of rupture of hydrogen bonds between adjacent molecular chains and without any decrease in the molecular weight of the nylon. A strength loss of 10–15% caused by photodegradation, however, is invariably associated with a considerable decrease in molecular weight because the initial attack occurs only at the surface of the fibre. Both forms of degradation are accompanied by an increase in the carboxyl end-group content and a decrease in the content of amine end-groups, but these changes are more marked with photodegradation (*21*). The protective effect of octyl gallate and certain azo dyes on the thermal breakdown of nylon fibres was examined by Fester, who observed that the loss in amine-group content was decreased and the yellowing was retarded but not completely prevented (*22*), presumably because the protective action depended on preferential oxidation of the octyl gallate or other antioxidant present.

Attack on the methylene group adjacent to the imino nitrogen of one amide group by free radicals arising from homolytic fission of another amide group nearby was postulated by Sharkey and Mochel to explain the photochemical decomposition of nylon (*23*). Detailed investigation of the products of thermal decomposition of n-pentylhexanamide by labelling with a radioactive ^{14}C isomer showed that hexanoic acid and its amide are formed from the carbonyl part of the original molecule and valeric acid and its aldehyde from the amino part. Considerable amounts of ammonia, carbon dioxide and carbon monoxide are also formed (*24*, *25*).

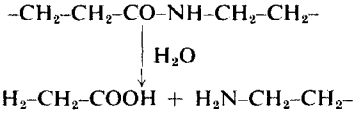
The yellowing of nylon 6.6 during thermal degradation was attributed by Rochas and Martin to the formation of pyrrole ring systems (*26*). The oxidation was believed to occur at the methylene groups adjacent to the carbonyl groups of the adipic acid residues to form αα′-diketoadipate residues. These are able to cyclise with ammonia or amine end-groups to form pyrroles. Marek and Lerch studied the effect of irradiating nylon 6.6

fabrics and solutions of the model compounds diacetylhexamethylenediamine and diethyladipodiamide in solution at 50°C in a fading lamp. The formation of pyrroles was detected (*27*) by means of the Ehrlich reagent. Hexamethylenediamine develops a strong Ehrlich coloration after exposure in solution for 8–48 days at 30°C, but acetylated derivatives do not react under these conditions and the presence of primary amine groups is essential. ε-Aminocaproic acid gives a strong initial reaction, but the Ehrlich test coloration decreases in intensity as the conditions of setting increase in severity. The adipic acid derivatives are oxidised, forming α-carbonyl groups, but show no positive Ehrlich reaction even in the presence of ammonia. The titanium dioxide added to nylon fibres as a delustrant can photosensitise the yellowing and degradation of the fibre on exposure to light, but small amounts of manganous salts suppress the formation of active oxygen.

The oxidative degradation of nylon 6.6 in aqueous systems has been studied recently. Even in aqueous solution the reaction proceeds by a free-radical mechanism (*28*) that is inhibited by benzoquinone or hydroquinone. It is postulated that hydroperoxides are formed in solution or on the fibre in the presence of trace metals and can act as initiators for the attack on the nylon. At pH 7–8, these hydroperoxides are capable of homolytic cleavage to give a pair of free radicals, but at other pH values a combination of homolytic and heterolytic processes occurs. Chain propagation may be catalysed by metal ions.

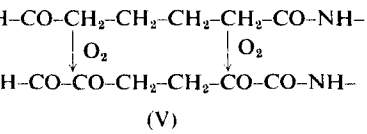
Some of the reactions that can occur during the thermal or photochemical breakdown of nylon are shown below. The mixture of substances formed as a final result of these changes is so complex that it is only practicable to indicate the kind of reactions that take place, rather than to account for every by-product. The oxidation process appears to proceed in at least three distinct stages: (*a*) attack by active oxygen or hydroperoxides at the methylene groups adjacent to the amide groups, (*b*) oxidation to αα′-diketo structures, and (*c*) cyclisation to pyrroles by condensation of the diketo residues with ammonia formed by hydrolysis of imino groups. There is also evidence that humid conditions and high temperatures can promote the partial polymerisation of pyrroles and certain carbonyl compounds to give yellow polymers of unknown structure (*29*, *30*).

Hydrolysis of Amide Groups



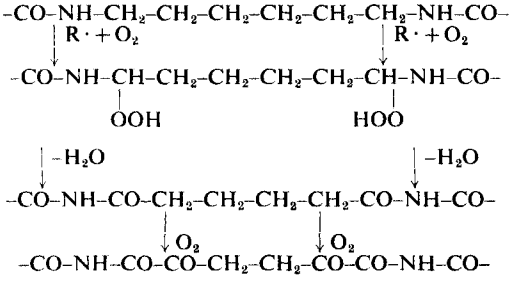
(IV)

Oxidation of Adipic Acid Residues in Nylon 6.6



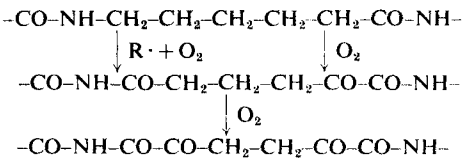
(V)

Oxidation of Hexamethylenediamine Residues in Nylon 6.6



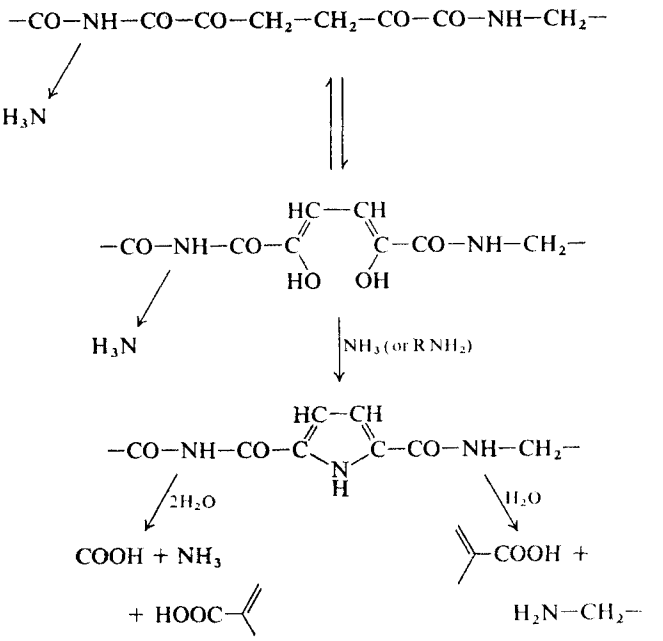
(VI)

Oxidation of Polycaprolactam

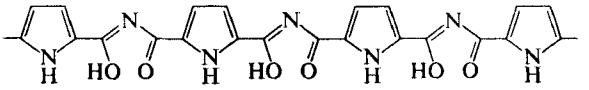


(VII)

Formation of Pyrroles from V, VI or VII



Polymer Containing Pyrrole Rings Conjugated through Imide Groups



Experimental

The effects of steam and dry-heat setting treatments differing in severity on the wet fastness of acid-dyed and backtanned nylon 6 and nylon 6.6 fabrics were compared. The yellowing of undyed fabrics during setting and the change in tensile strength of dyed and undyed samples were also measured so as to relate the degradation of the fibre and the tanning agent to the loss in effectiveness of the backtanning treatment.

Samples of nylon 6.6 and nylon 6 taffeta fabrics were cut into 2-g squares and the direction of the weft was marked. Sets of squares of total weight 500 g from each fabric were treated at a liquor:goods ratio of 40:1 for 15 min at 50°C with 1·2% Lissapol D (ICI) in 3% ammonium acetate and then dyed with 1·8% C.I. Acid Blue 25 for 1 h at 95°C from the same solution. (All quantities above and below are expressed on weight of fabric.) One portion of the dyed material (100 g) was after-treated with 2% tannic acid and 4% formic acid for 30 min at the same liquor:goods ratio, 1% tartar emetic was added and the treatment was continued for a further 15 min. A further portion (100 g) was treated with 3% Taninol WR 200 (ICI) and 4% formic acid for 30 min at a liquor:goods ratio of 40:1. In both instances the treatment temperatures were 65°C for nylon 6

and 95°C for nylon 6.6. Further portions of dyed and undyed samples were aftertreated with a large excess of the tanning agents, i.e. 50% tannic acid and 25% tartar emetic, or 20% Taninol WR 200 (100 g dyed and 100 g undyed by each method), using the same conditions of application. The remaining portions formed the dyed and undyed controls.

These pretreatments gave a total of 200 sets of dyed or undyed pairs of samples forming 25 repeats of eight different treatments. Twelve of the repeats were steam-set in a Barton horizontal steamer for 0·5, 1, 2 and 3 h at 15, 20 and 25 lb/in² and a further twelve were dry-heat set in a Benz laboratory baker, leaving the final series of eight patterns as unset controls. Six of the dry-heat treatments lasted for 30 s at temperatures ranging from 140 to 210°C (nylon 6) or 170 to 230°C (nylon 6.6) and the other six for times ranging from 5 to 120 s at 190°C (nylon 6) or 210°C (nylon 6.6) respectively. The conditions of setting ranged from very mild to very severe, in order to assess the effects of practical processes as well as extreme conditions not normally encountered in practice.

One fabric in each of the dyed sets was tested for colour fastness to water and ISO 3 washing tests The results of these tests are given in Tables 1–4. The reflectance at 380 nm of one fabric in each of the undyed sets was measured on a Hardy spectrophotometer, using the corresponding untreated control fabric as the reference specimen. The reflectance measurements (Tables 5–8) were converted to Kubelka–Munk K/S values and multiplied by 100 to express them in a convenient form. The other fabric in each pair of dyed and undyed fabrics was tested for weft tensile strength and extension at break on a Goodbrand tester. The losses (%) in tensile strength and extensibility were calculated using the measurements of the properties of the appropriate controls. The trends of the changes in extensibility followed closely the trends of the losses in strength and only the latter results are given in Tables 9–12. To simplify the headings in the Tables, the expressions Normal Taninol WR, Normal Tannic Acid, Excess Taninol WR and Excess Tannic Acid have been used to denote the conventional aftertreatments and the corresponding treatments with a large excess of the agents.

Discussion

The relations between the variables presence or absence of dye, type of nylon fibre, type and amount of backtanning agent, type of heat-setting medium, time and temperature of setting and the wet fastness and physical properties of the fabric are fairly complicated and it is convenient therefore to discuss the relations within each set of results before considering the comparison of wet fastness, yellowing and degradation.

WET FASTNESS OF DRY-SET NYLON 6.6 (TABLE 1)

There was a significant decrease in wet fastness of the dyed control during the setting treatment, the average of the ISO 3 washing-fastness ratings decreasing from 3·33 before setting to 2·67 after 120 s at 210°C and the average water-fastness rating decreasing from 3·33 to 2·50 after 30 s at 230°C. The backtanned samples also had lower wet fastness, but not to the level of the dyed control before setting. The decrease in fastness of the backtanned dyeings appeared to occur mainly in the early stages of the dry-setting treatment, especially with those samples treated with excess of the agent. The samples with the normal amount of agent present gave slightly better results on dry-set nylon 6.6, and the tannic acid and tartar emetic aftertreatment gave more durable results than those obtained with Taninol WR.

WET FASTNESS OF DRY-SET NYLON 6 (TABLE 2)

The wet fastness of the dye was considerably lower on the dyed nylon 6 control than on the dyed nylon 6.6 control before setting and the loss on setting was of the same magnitude, so that the wet fastness of the dyed nylon 6 after dry setting was still inferior. Similar results were obtained with the backtanned dyeings. The improvement in wet fastness on application of the tanning agents to nylon 6 was less than that with nylon 6.6 and the rate of loss of wet fastness of the aftertreated nylon 6 was higher during setting. Hence the wet fastness of the dyed and aftertreated nylon 6 returned to its original value (before setting) after dry-heat treatment for 60 s at 190°C. As on nylon 6.6, the natural tannin treatment gave more durable results on nylon 6 than those obtained with the syntan.

TABLE 1

Wet-fastness Properties of Dry-set Nylon 6.6

Dry-setting conditions		Excess Taninol WR			Normal Taninol WR			Dyed only			Normal tannic acid			Excess tannic acid		
Time (s)	Temp. (°C)	E	N	W	E	N	W	E	N	W	E	N	W	E	N	W
ISO 3 Washing																
Not heat-set		4–5G	5	5	5	5	5	4	4	2	5	5	5	4DG	5	5
5	210	4–5G	5	4–5	5	5	4–5	4	4	2	5	5	5	3DG	5	5
10	210	4–5G	4–5	4	5	5	4–5	4	4	2	5	5	5	3DG	5	4
20	210	4–5G	4–5	4	5	5	4–5	4	3–4	2	5	5	5	3DG	5	4
30	210	4–5G	4–5	3–4	5	5	4	3–4	3–4	2	5	5	4–5	3DG	4	3–4
40	210	4–5G	4–5	3–4	5	5	4	3–4	3–4	2	5	5	4–5	2–3DG	4	3–4
60	210	4–5G	4–5	4	5	4–5	4	3–4	3–4	1–2	5	4–5	4–5	3–4DG	3–4	3–4
120	210	4–5G	4–5	3–4	5	4–5	4	3–4	3	1–2	5	4–5	4	2–3DG	4	3
30	170	4–5G	5	5	5	5	5	4	4	2	5	5	5	4DG	5	5
30	190	4–5G	5	4–5	5	5	5	3–4	4	2	5	5	5	4DG	5	4–5
30	200	4–5G	4–5	3–4	5	5	4–5	3–4	3–4	2	5	5	5	3–4DG	4–5	4
30	210	4–5G	4–5	3–4	5	5	4	3–4	3–4	2	5	5	4–5	3DG	4	3–4
30	220	4G	4	3	5	5	4	3–4	3–4	2	4–5	5	4–5	3DG	4	3–4
30	230	4G	4	3	5	4–5	3–4	3–4	3–4	2	4–5	5	4–5	2–3DG	4	3
Water Fastness																
Not heat-set		4–5D	5	5	5	5	5	4	3	3	5	5	5	4–5D	5	5
5	210	4–5D	4–5	4–5	5	5	5	4	2–3	2–3	5	5	5	4–5D	5	5
10	210	4–5D	4	4	5	5	5	4	2–3	2–3	5	5	5	4–5D	5	5
20	210	4D	4	3–4	5	4–5	5	4	2	2	5	5	5	4–5D	5	5
30	210	4D	3–4	3–4	5	4–5	4–5	3–4	2	2	5	5	5	4DG	5	5
40	210	4D	3–4	3–4	5	4–5	4–5	3–4	2–3	2	5	5	5	4DG	5	5
60	210	4D	3–4	3	5	4–5	4–5	3–4	2	2	5	5	5	4DG	4–5	4–5
120	210	4D	3	3	5	4	4	4	2–3	2–3	5	5	5	4DG	4–5	4–5
30	170	4–5D	5	5	5	5	5	4	3	3	5	5	5	4–5D	5	5
30	190	4–5D	4–5	4–5	5	5	5	4	3	2–3	5	5	5	4–5D	5	5
30	200	4–5D	4–5	4	5	4–5	5	4	2–3	2–3	5	5	5	4–5D	5	5
30	210	4D	4	3–4	5	4–5	4–5	3–4	2	2	5	5	5	4DG	4–5	5
30	220	4D	3–4	3	5	4	4–5	3–4	2	2	5	5	4–5	4DG	4–5	4–5
30	230	4D	2–3	2–3	5	4	4	3–4	2	2	5	5	4–5	3–4DG	4	4

E—Effect on colour, N—Staining of nylon, W—Staining of wool

TABLE 2

Wet fastness Properties of Dry-set Nylon 6

Dry-setting conditions Time (s)	Temp. (°C)	Excess Taninol WR E	N	W	Normal Taninol WR E	N	W	Dyed only E	N	W	Normal tannic acid E	N	W	Excess tannic acid E	N	W
							ISO 3 Washing									
Not heat-set		4	4	2–3	4	4–5	2–3	3	3–4	2	5	5	4–5	3–4D	3–4	2–3
5	190	3–4	4	2–3	4	4	2–3	3	3–4	2	4–5	4–5	4	3–4D	3–4	2–3
10	190	3–4	3–4	2–3	3–4	4	2–3	3	3–4	2	4–5	4–5	3–4	3D	3	2
20	190	3–4	3–4	2–3	3–4	3–4	2–3	3	3	2	4–5	4	3–4	3D	3	2
30	190	3	3–4	2–3	3–4	3–4	2	3	3	2	4–5	4	3	2–3DG	3	1–2
40	190	3	3	2	3	3	2	3	3	1–2	4	4	3	2DG	3	1–2
60	190	3	3	2	3	3	2	2–3	3	1–2	4	3–4	2–3	2DG	2–3	1
120	190	3	3	2	3	3	2	2–3	2–3	1–2	3–4	3–4	2–3	1–2DG	2–3	1
30	140	4	4	2–3	4	4	2–3	3	3–4	2	5	5	4–5	3–4D	3–4	2–3
30	160	3–4	4	2–3	3–4	4	2–3	3	3–4	2	5	4	4	3DG	3–4	2
30	170	3–4	3–4	2–3	3–4	3–4	2	3	3	2	4–5	4	3–4	3DG	3	2
30	190	3	3–4	2–3	3–4	3–4	2	3	3	2	4–5	4	3	2–3DG	3	1–2
30	200	2–3	3	2	3	3–4	2	2–3	2–3	1–2	4	4	2–3	1–2DG	3	1–2
30	210	2	3	2	3	3	1–2	2	2–3	1–2	3	3–4	2	1DG	2–3	1–2
							Water Fastness									
Not heat-set		4–5D	4–5	4–5	4–5	4	4	3–4	3	2	4–5	4–5	4	4–5D	4–5	4
5	190	4–5D	4	3–4	4	3–4	3–4	3–4	3	2	4–5	4	4	4–5D	4	4
10	190	4–5D	3	3	4	3–4	3	3–4	3	2	4	4	4	4D	4	3–4
20	190	4D	2–3	2–3	3–4	3	2–3	3–4	2–3	2	4	3–4	3–4	4D	3–4	3–4
30	190	3–4D	2–3	2–3	3–4	3	2–3	3	2–3	2	4	3–4	3–4	3–4DG	3–4	3
40	190	3–4D	2–3	2	3	2–3	2	3	2–3	1–2	4	3–4	3	3–4DG	3–4	3
60	190	3D	2–3	2	3	2–3	1–2	3	2–3	1–2	3–4	3	3	3DG	3–4	3
120	190	3D	2–3	2	3	2–3	1–2	2–3	2	1–2	3–4	3	3	2–3DG	3–4	3
30	140	4–5D	4	4	4–5	3–4	3–4	3–4	3	2	4	4	3–4	4–5D	4–5	3–4
30	160	4D	3–4	3	4	3–4	3–4	3	3	2	4	4	3–4	4D	4	3
30	170	4D	3	2–3	4	3	3	3	2–3	2	4	3–4	3–4	4D	4	3
30	190	3–4D	2–3	2–3	3–4	3	2–3	3	2–3	2	4	3–4	3–4	3–4DG	3–4	3
30	200	3D	2–3	2	3–4	3	2	2–3	2	2	3–4D	3	3–4	3DG	3–4	2–3
30	210	3D	2	2	3	2–3	2	2–3	2	1–2	3–4D	3	3	2DG	3	2

E—Effect on colour, N—Staining of nylon, W—Staining of wool

WET FASTNESS OF STEAM-SET NYLON 6.6 (TABLE 3)

The wet fastness of the dyed control decreased during steaming, the effect of steaming for 2 h at 25 lb/in² or 3 h at 20 lb/in² being equivalent to that of dry setting for 120 s at 210°C or 30 s at 230°C. Steam setting for 3 h at 25 lb/in² reduced the wet fastness of the backtanned dyeings to a level slightly below that of the dyed control before setting. The syntan treatment was slightly more resistant to steam treatment than the natural-tannin treatment. The durability conferred by the normal and excessive amounts of the tanning agents was similar. The effect of dry setting for 120 s at 210°C on the fastness to ISO 3 washing of the backtanned dyeings was equivalent to steam setting for 1 h at 20 lb/in² or 2 h at 15 lb/in². The effect of dry setting for 30 s at 230°C on the water fastness of the backtanned samples was equivalent to that caused by steaming for only 0·5 h at 15 lb/in².

TABLE 3

Wet-fastness Properties of Steam-set Nylon 6.6

Steam-setting conditions Time (h)	Pressure (lb/in²)	Excess Taninol WR E	N	W	Normal Taninol WR E	N	W	Dyed only E	N	W	Normal tannic acid E	N	W	Excess tannic acid E	N	W
							ISO 3 Washing									
Not heat-set		4–5G	5	5	5	5	5	4	4	2	5	5	5	4DG	5	5
0·5	15	4–5G	5	4–5	5	5	4	4	4	2	5	5	4–5	4DG	4–5	4
1	15	4–5G	4–5	4	5	4–5	3–4	4	4	2	5	5	4	4DG	4–5	4
2	15	4–5G	4	4	5	4–5	3–4	4	3–4	2	5	4–5	3–4	3–4DG	4	3–4
3	15	4–5G	4	4	5	4–5	3–4	4	3–4	1–2	5	4–5	3–4	3–4	4	3
0·5	20	4–5G	5	4–5	5	5	4	4	4	2	5	5	4	4DG	4–5	3–4
1	20	4–5G	4–5	4	5	5	3–4	4	3–4	1–2	5	4–5	3–4	3–4DG	4	3
2	20	4–5G	4	4	5	4–5	3–4	3–4	3–4	2	5	4–5	3	3–4DG	4	3
3	20	4G	4	3–4	5	4–5	3	3–4	3	1–2	4–5	4	3	3DG	3–4	2–3
0·5	25	4–5G	4–5	3	5	5	3–4	4	3–4	2	5	4–5	3–4	3–4DG	3–4	3
1	25	4–5G	4–5	3	5	4–5	3	4	3	1–2	4–5	4	3	3DG	3–4	2–3
2	25	4G	4	3	5	4–5	3	3–4	3	1–2	4–5	4	3	2–3DG	3	2
3	25	4G	4	2–3	4–5	4	2–3	3–4	2–3	1	4–5	3–4	2–3	2–3DG	3	2
							Water Fastness									
Not heat-set		4–5D	5	5	5	5	5	4	3	3	5	5	5	4–5D	5	5
0·5	15	4–5D	4	3	5	4–5	4–5	4	3	3	5	4–5	4–5	4–5D	4–5	4–5
1	15	4–5D	3	2–3	5	4	4	4	2–3	3	5	4–5	4–5	4D	3–4	3–4
2	15	4–5D	3	2–3	5	4	4	4	2–3	2–3	5	4	4	4D	3	3
3	15	4–5D	2–3	2	5	3–4	3–4	3–4	2–3	2–3	5	3–4	3–4	3–4DG	2–3	3
0·5	20	4–5D	3–4	3	5	4–5	4–5	4	3	2–3	5	4–5	4	4D	3–4	3
1	20	4–5D	2–3	2–3	5	4	4	4	2–3	2	5	4	4	4D	2–3	2–3
2	20	4–5D	2	2	5	3–4	3	3–4	2–3	2	4–5	3–4	3–4	3–4DG	2	2
3	20	4DG	2	2	4–5	3	2–3	3–4	2	2	4–5	3	2–3	3–4DG	2	2
0·5	25	4–5D	2–3	2	5	3–4	3	4	2–3	2–3	4–5	3	3	3–4DG	3	2–3
1	25	4–5D	2	2	4–5	2–3	2–3	3–4	2	2	4–5	2–3	3	3–4DG	2	2
2	25	4DG	2	2	4–5	2	2–3	3–4	2	2	4–5	2–3	2–3	3DG	2	2
3	25	4DG	2	1–2	4	2	2–3	3–4	2	2	4	2	2	3DG	1–2	1–2

E—Effect on colour, N—Staining of nylon, W—Staining of wool

WET FASTNESS OF STEAM-SET NYLON 6 (TABLE 4)

The initial wet fastness of the dyed nylon 6 control was slightly inferior to that of a similar dyeing on nylon 6.6 and the loss in wet fastness on steam setting was similar in magnitude on both fibres. The effect on wet fastness of steam setting for 3 h at 25 lb/in² was equivalent to that obtained under the most severe dry-setting conditions examined. The natural tannin was more effective than the syntan in improving the wet-fastness properties on nylon 6 but both agents were less effective on nylon 6 than on nylon 6.6 fibres and the durability to steam setting of the syntan treatment was better than that of the natural tannin on both types of nylon. The influence on wet fastness of the nylon 6 dyeings under the most severe conditions of dry setting was equivalent to that of steam setting for 0·5 h at 20 lb/in² or 1 h at 15 lb/in².

TABLE 4

Wet-fastness Properties of Steam-set Nylon 6

Steam-setting conditions		Excess Taninol WR			Normal Taninol WR			Dyed only			Normal tannic acid			Excess tannic acid		
Time (h)	Pressure (lb/in²)	E	N	W	E	N	W	E	N	W	E	N	W	E	N	W
							ISO 3 Washing									
Not heat-set		4	4	2–3	4	4–5	2–3	3	3–4	2	5	5	4–5	3–4D	3–4	2–3
0·5	15	4	4	2–3	4	4	2–3	3	3–4	2	4–5	5	4	2DG	3	2–3
1	15	4	4	2–3	4	3–4	2–3	2–3	3–4	2	4	4–5	4	1–2DG	2	2
2	15	3–4	4	2–3	3–4	3–4	2–3	2–3	3	2	3–4	4	3–4	1–2DG	2	2
3	15	3–4	4	2–3	3	3	2–3	2–3	3	2	3	4	3	1DG	1–2	1–2
0·5	20	4	4	2–3	4	3–4	2–3	2–3	3–4	2	4	4–5	4–5	1–2DG	3	2–3
1	20	3–4	4	2–3	3–4	3–4	2–3	2–3	3	2	3–4	4	4	1–2DG	2–3	2–3
2	20	3–4	3–4	2–3	3	3–4	2–3	2	2–3	2	3	4	3–4	1DG	1–2	2
3	20	3–4	3–4	2	2–3	3	2–3	2	2–3	1–2	2–3	3–4	3	1DG	1–2	1–2
0·5	25	3–4	4	2–3	3–4	3–4	2–3	2–3	3	2	4	4–5	4	1–2DG	2	2–3
1	25	3–4	3–4	2–3	3	3–4	2–3	2	2–3	2	3–4	3–4	3	1DG	1–2	1–2
2	25	3	3–4	2	3	3	2	2	2–3	1–2	2–3	3–4	2–3	1DG	1	1–2
3	25	3	3	2	2–3	3	2	2	2	1–2	2	3	2	Sample destroyed		
							Water Fastness									
Not heat-set		4–5D	4–5	4–5	4–5	4	4	3–4	3	2	4–5	4–5	4	4–5D	4–5	4
0·5	15	4–5D	3–4	3–4	4–5	4	3–4	3–4	2–3	2	4	3–4	3–4	3–4D	3–4	3–4
1	15	4D	3	3	4–5	4	3	3	2	2	4	3	3	3DG	3	3
2	15	4D	3	2–3	4	3	2–3	3	2	2	4	3	2–3	2–3DG	3	3
3	15	3–4D	2–3	2–3	3–4	2–3	2	2–3	2	2	3–4	2–3	2–3	2DG	2–3	2–3
0·5	20	4D	3	3	4–5	4	3	3–4	2–3	2	4	3	3	3DG	3	2–3
1	20	3–4D	3	2–3	4	3–4	2–3	3	2	2	4	3	2–3	2DG	2–3	2–3
2	20	3–4D	2–3	2–3	4	3	2	2–3	2	2	4	2–3	2–3	1–2DG	2–3	2
3	20	3D	2–3	2	3–4	2–3	2	2–3	2	2	3–4	2	2	1DG	2	2–3
0·5	25	4D	3	2–3	4	3–4	2–3	3	2	2	4	3	3	2–3DG	2–3	2
1	25	3–4D	2–3	2	3–4	3	2	2–3	2	2	3–4	2–3	2–3	2DG	2	2
2	25	3D	2	2	3	2–3	2	2–3	2	2	3	2	2	1–2DG	2	1–2
3	25	3D	2	2	3	2	1–2	2–3	2	1–2	3	2	2	Sample destroyed		

E—Effect on colour, N—Staining of nylon, W—Staining of wool

YELLOWING OF DRY-SET NYLON 6.6 (TABLE 5)

The yellowing of undyed nylon 6.6 during dry-heat setting was slight (Kubelka–Munk value only 2·5 after 120 s at 210°C) in comparison with that caused by application of the natural tannin (45) or the syntan (77), or the increase in yellowing during heat setting for 120 s at 210°C of the samples treated with tannic acid (45 to 277) or Taninol WR (77 to 143). At 210°C the extent of yellowing increased slowly in the early stages, but the rate increased with time of setting. Similarly, yellowing was very slight below 200°C and the rate of yellowing with temperature increased rapidly with temperature, which was indicative of a high energy of activation of the yellowing reaction.

The results gave the expected linear relation between log (K/S) and reciprocal temperature, but the data were insufficient, especially for steam setting, to yield accurate values for this energy of activation. The yellowing produced by application of the agents was greater with the syntan than with the natural tannin, but the latter agent caused a higher rate of increase in depth of discoloration with time or temperature of setting.

TABLE 5

Yellowing of Dry-set Nylon 6.6

Dry-setting conditions		Reflectance (%)			Kubelka–Munk value (100 K/S)		
Time (s)	Temp. (°C)	Excess Taninol WR	Undyed only	Excess tannic acid	Excess Taninol WR	Undyed only	Excess tannic acid
Not heat-set		31	100	40	77	0	45
5	210	28·5	100	31	90	0	77
10	210	26·5	100	30·5	102	0	79
20	210	25	97	25	112	0·05	112
30	210	25	95	25	112	0·13	112
40	210	24·5	93	24·5	116	0·26	116
60	210	24·5	90	18·5	116	0·56	180
120	210	21·5	80	13·5	143	2·50	277
30	170	30	100	40	82	0	45
30	190	28·5	100	34	90	0	64
30	200	25	99	29	112	0·01	87
30	210	25	95	25	112	0·13	112
30	220	24	92·5	18·5	120	0·30	180
30	230	23	86	14	129	1·14	264

YELLOWING OF DRY-SET NYLON 6 (TABLE 6)

Undyed nylon 6 yellowed to a greater extent than undyed nylon 6.6 at a given time and temperature of dry-heat treatment, although both types of backtanning process caused less yellowing of nylon 6 than of nylon 6.6 on application and after setting at a given degree of severity of treatment. As on nylon 6.6, the yellowing by the syntan was greater during application than after setting, but the increase in yellowness during setting was greater for the natural tannin.

TABLE 6

Yellowing of Dry-set Nylon 6

Dry-setting conditions		Reflectance (%)			Kubelka–Munk value (100 K/S)		
Time (s)	Temp. (°C)	Excess Taninol WR	Undyed only	Excess tannic acid	Excess Taninol WR	Undyed only	Excess tannic acid
Not heat-set		52	100	63	22	0	11
5	190	51	100	58·5	24	0	15
10	190	51·5	100	54·5	23	0	19
20	190	48·5	96·5	49·5	27	0·06	26
30	190	49·5	95	45·5	26	0·13	33
40	190	45	90	41·5	34	0·56	41
60	190	45	85·5	38	34	1·23	51
120	190	42·5	75·5	31	39	3·98	77
30	140	52	100	55·5	22	0	18
30	160	51	100	52·5	24	0	21
30	170	51·5	98·5	52	23	0·01	22
30	190	49·5	95	45·5	26	0·13	33
30	200	46	83	34	32	1·74	64
30	210	40·5	63	24	44	10·86	120

YELLOWING OF STEAM-SET NYLON 6.6 (TABLE 7)

Yellowing of the undyed control was negligible during steam setting, much less than during the dry setting of nylon 6.6. The syntan caused more discoloration than the natural tannin, but during steaming both samples caused further yellowing at a similar rate, which was greater than that of the undyed control during steam setting. The original discoloration of the nylon 6.6 on treatment with the tanning agents was doubled after steam setting for 2 h at 25 lb/in² or 3 h at 20 lb/in² (syntan), or for 3 h at 25 lb/in² (natural tannin).

TABLE 7

Yellowing of Steam-set Nylon 6.6

Steam-setting conditions		Reflectance (%)			Kubelka–Munk value (100 K/S)		
Time (h)	Pressure (lb/in²)	Excess Taninol WR	Undyed only	Excess tannic acid	Excess Taninol WR	Undyed only	Excess tannic acid
Not heat-set		31	100	40	77	0	45
0·5	15	25·5	100	37·5	109	0	52
1	15	25	100	35·5	112	0	59
2	15	22·5	99	34	133	0·01	64
3	15	22	98·5	30	138	0·01	82
0·5	20	25	100	36	113	0	57
1	20	23·5	100	33	125	0	68
2	20	23·5	98·5	31	125	0·01	77
3	20	21	95	30·5	149	0·13	79
0·5	25	25·5	100	35	109	0	60
1	25	23	100	33·5	129	0	66
2	25	21·5	97·5	28·5	143	0·03	90
3	25	19	94	27·5	173	0·19	96

YELLOWING OF STEAM-SET NYLON 6 (TABLE 8)

Yellowing of the undyed nylon 6 control was negligible, far less than on dry setting, although the effect was slightly greater than on nylon 6.6 at a given time and pressure of setting. Yellowing of the backtanned nylon 6 samples. however, was less than that of nylon 6.6 under the same steaming conditions. The original discoloration caused by the syntan was double that caused by the natural tannin, but yellowing caused by this increased more rapidly on steaming. The original effect of the syntan was doubled after dry setting for 30 s at 210°C or steaming for only 0·5 h at 15 lb/in², and the original yellowing by tannic acid was 7 to 8 times as much after dry setting for 30 s at 200–210°C or steam setting for 3 h at 25 lb/in².

TABLE 8

Yellowing of Steam-set Nylon 6

Steam-setting conditions		Reflectance (%)			Kubleka–Munk value (100 K/S)		
Time (h)	Pressure (lb/in²)	Excess Taninol WR	Undyed only	Excess tannic acid	Excess Taninol WR	Undyed only	Excess tannic acid
Not heat-set		52	100	63	22	0	11
0·5	15	43	100	44	38	0	36
1	15	35·5	100	40·5	59	0	44
2	15	33·5	100	37·5	66	0	52
3	15	33	98	34·5	68	0·02	62
0·5	20	38	100	39	51	0	48
1	20	35·5	100	37	59	0	54
2	20	34·5	98	34	62	0·02	64
3	20	33	94·5	31·5	68	0·16	74
0·5	25	38	100	37·5	51	0	52
1	25	37·5	98	34	52	0·02	64
2	25	35	96	33	60	0·08	68
3	25	32	90	30	72	0·56	82

TENSILE STRENGTH OF DRY-SET NYLON 6.6 (TABLE 9)

The dyeing and normal backtanning processes had a negligible effect on the tensile strength of nylon 6.6 but were accompanied by a loss in extensibility of about 10%. Treatment with excessive amounts of the tanning agents caused a loss in strength of 7–8% and a greater loss in extensibility. Dry setting of untreated nylon 6.6 for 120 s at 210°C decreased the strength by 27% and for 30 s at 230°C by 40%. The tensile strength decreased more rapidly in the early stages of treatment while the regain moisture was being evaporated from the fibre and the rate of loss was lower later. Both of the symptoms of degradation observed, viz. loss in strength and yellowing, showed a rapid rise in rate with increasing temperature, which demonstrated the high energy of activation of the decomposition reactions. The rate of loss in strength was higher for the undyed control than for the dyed control, but the dyed and undyed samples after backtanning were degraded at similar rates. The rate of loss of tensile strength was considerably greater in the presence of excess of tanning agent than for the normal processes, and the loss in strength of the samples containing the natural tannin and tartar emetic was more than double that of the syntan-treated material.

TABLE 9

Tensile Strength of Dry-set Nylon 6.6

Dry-setting conditions		Undyed	Dyed	Dyed	Undyed	Dyed	Dyed	Dyed	Undyed
Time (s)	Temp. (°C)	Excess Taninol WR	Excess Taninol WR	Normal Taninol WR	Undyed only	Dyed only	Normal tannic acid	Excess tannic acid	Excess tannic acid
					Tensile strength (kg)				
Not heat-set		39·2	42·8	42·2	42·6	43·8	40·8	43·4	39·6
5	210	39·6	41·4	44·4	39·1	45·8	43·8	35·1	31·1
10	210	38·5	38·7	38·5	40·5	43·3	36·4	33·6	27·5
20	210	38·7	37·5	39·0	38·5	40·1	37·0	30·8	28·3
30	210	35·8	37·6	38·8	36·6	40·3	35·1	30·7	25·7
40	210	33·9	36·0	37·8	35·4	37·6	30·0	28·4	25·0
60	210	32·0	34·5	36·9	32·4	38·9	25·8	25·9	23·3
120	210	30·8	33·0	36·3	31·3	36·3	24·5	21·4	19·3
30	170	39·5	41·5	41·1	41·2	42·5	39·6	40·4	36·9
30	190	40·1	40·6	40·4	39·8	41·7	38·3	37·0	33·1
30	200	40·4	38·6	39·4	38·4	41·1	37·2	33·5	27·2
30	210	35·8	37·6	38·8	36·6	40·3	35·1	30·7	25·7
30	220	33·8	33·3	39·0	33·6	39·6	33·2	25·0	19·3
30	230	30·1	34·3	35·8	25·4	35·6	27·4	21·7	19·0
					Loss in tensile strength (%)				
Not heat-set		8*	0*	1*	UC	0*	4*	0*	7*
5	210	0	3	0	8	0	0	19	21
10	210	2	10	9	5	1	11	23	31
20	210	1	12	8	10	8	9	29	28
30	210	9	12	8	14	8	14	29	35
40	210	14	16	10	17	14	27	35	37
60	210	18	19	13	24	11	37	39	41
120	210	21	23	14	27	17	40	51	51
30	170	0	3	3	3	3	3	7	6
30	190	0	5	4	7	5	6	15	15
30	200	0	10	7	10	6	9	23	31
30	210	9	12	8	14	8	14	29	35
30	220	14	22	8	21	10	19	42	51
30	230	23	20	15	40	19	32	50	52

*Based on untreated control (UC). Other losses are based on the appropriate unset control

TENSILE STRENGTH OF DRY-SET NYLON 6 (TABLE 10)

All the trends discussed in the previous section for the dry setting of dyed, undyed and backtanned nylon 6.6 were confirmed on nylon 6 to a greater degree, since the strength losses on nylon 6 were considerably higher in all instances. This behaviour is consistent with the much greater tendency to yellowing of nylon 6 during dry-heat setting.

TABLE 10

Tensile Strength of Dry-set Nylon 6

Dry-setting conditions		Undyed	Dyed	Dyed	Undyed	Dyed	Dyed	Dyed	Undyed
Time (s)	Temp. (°C)	Excess Taninol WR	Excess Taninol WR	Normal Taninol WR	Undyed only	Dyed only	Normal tannic acid	Excess tannic acid	Excess tannic acid
					Tensile strength (kg)				
Not heat-set		27·7	30·1	29·9	30·0	31·8	28·2	31·5	27·7
5	190	28·1	27·6	28·0	29·6	30·1	26·2	26·3	26·6
10	190	25·7	27·0	27·3	26·6	29·6	24·4	22·1	24·5
20	190	25·4	26·8	26·2	23·9	28·4	23·6	21·3	23·6
30	190	24·9	26·0	25·2	23·3	27·1	23·2	20·8	21·6
40	190	24·2	25·0	25·7	23·2	27·6	21·3	18·5	20·9
60	190	22·9	24·7	25·2	20·1	27·4	21·9	17·5	17·0
120	190	21·9	20·0	24·2	19·3	25·4	21·3	12·1	13·7
30	140	27·8	28·9	29·8	29·5	29·7	26·8	29·0	27·6
30	160	27·4	27·5	27·9	28·1	27·5	24·7	27·4	27·4
30	170	27·2	26·5	26·1	25·9	27·6	23·9	24·5	25·2
30	190	24·9	26·0	25·2	23·3	27·1	23·2	20·8	21·6
30	200	20·4	21·4	20·8	19·7	21·6	20·7	18·2	17·0
30	210	15·1	10·2	15·5	13·3	17·0	14·6	8·9	8·3

TABLE 10—cont.

Tensile Strengh of Dry-set Nylon 6

Dry-setting conditions		Undyed	Dyed	Dyed	Undyed	Dyed	Dyed	Dyed	Undyed
Time (s)	Temp. (°C)	Excess Taninol WR	Excess Taninol WR	Normal Taninol WR	Undyed only	Dyed only	Normal tannic acid	Excess tannic acid	Excess tannic acid
				Loss in tensile strength (%)					
Not heat-set		8*	0*	0*	UC	0*	6*	0*	8*
5	190	0	8	6	1	5	7	16	4
10	190	7	10	9	11	7	13	30	12
20	190	8	11	12	20	11	16	32	15
30	190	10	14	16	22	15	18	34	22
40	190	13	17	14	23	13	24	42	25
60	190	17	18	16	33	14	22	44	39
120	190	21	33	19	36	20	24	62	51
30	140	0	4	0	2	7	5	8	0
30	160	1	9	7	6	14	12	13	1
30	170	2	12	13	14	13	15	22	9
30	190	10	14	16	22	15	18	34	22
30	200	26	29	30	34	32	27	42	39
30	210	45	66	48	56	46	48	72	70

*Based on untreated control (UC). Other losses are based on the appropriate unset control

TENSILE STRENGTH OF STEAM-SET NYLON 6.6 (TABLE 11)

The tensile strength and extensibility of the dyed and undyed nylon 6.6 controls were hardly changed by steam setting (treatment for 3 h at 25 lb/in² caused only 6–7% loss in strength, equivalent to dry setting for only 30 s at 190–200°C) but the effect of steam setting on the backtanned samples approached that of dry-heat setting after backtanning.

TABLE 11

Tensile Strength of Steam-set Nylon 6.6

Steam-setting conditions		Undyed	Dyed	Dyed	Undyed	Dyed	Dyed	Dyed	Undyed
Time (h)	Pressure (lb/in²)	Excess Taninol WR	Excess Taninol WR	Normal Taninol WR	Undyed only	Dyed only	Normal tannic acid	Excess tannic acid	Excess tannic acid
				Tensile strength (*kg*)					
Not heat-set		39·2	42·8	42·2	42·6	43·8	40·8	43·4	39·6
0·5	15	38·7	39·5	39·6	42·4	43·8	38·8	37·0	24·0
1	15	36·9	36·9	36·4	43·3	42·8	35·4	30·6	20·8
2	15	34·5	33·8	35·1	42·3	44·0	33·2	28·1	19·9
3	15	33·8	29·7	34·2	41·6	44·1	32·2	27·3	18·1
0·5	20	37·9	38·2	39·1	43·7	43·9	36·5	35·3	23·4
1	20	35·6	34·3	36·9	42·5	44·8	32·7	28·8	20·6
2	20	33·2	31·4	35·5	42·7	44·4	32·0	25·9	17·5
3	20	32·4	30·6	34·0	41·0	41·4	30·3	24·5	17·0
0·5	25	38·3	37·9	38·7	42·8	44·0	36·9	28·4	20·9
1	25	34·1	34·1	36·8	42·1	44·2	34·6	22·8	17·5
2	25	33·2	32·8	35·3	41·3	42·4	32·9	21·2	15·7
3	25	32·0	27·5	32·1	39·8	41·3	30·1	20·1	15·0
				Loss in tensile strength (%)					
Not heat-set		8*	0*	1*	UC	0*	4*	0*	7*
0·5	15	1	8	6	0	0	5	15	39
1	15	6	14	14	0	2	13	30	48
2	15	12	21	17	0	0	19	35	50
3	15	14	31	19	2	0	21	37	54
0·5	20	3	11	7	0	0	11	19	41
1	20	9	20	13	0	0	20	34	48
2	20	15	27	16	0	0	22	40	56
3	20	17	29	20	4	5	26	44	57
0·5	25	2	11	8	0	0	10	35	47
1	25	13	20	13	1	0	15	47	56
2	25	15	23	16	3	3	19	51	60
3	25	18	36	24	7	6	26	53	62

*Based on untreated control (UC). Other losses are based on the appropriate unset control

TENSILE STRENGTH OF STEAM-SET NYLON 6 (TABLE 12)

The steam setting of nylon 6 caused similar effects on tensile strength and extensibility to those observed with nylon 6.6, but modification of the nylon 6 was greater. The dyed and undyed controls were only slightly degraded but the backtanned samples suffered considerable losses in strength and extensibility.

TABLE 12

Tensile Strength of Steam-set Nylon 6

Steam-setting conditions		Undyed	Dyed	Dyed	Undyed	Dyed	Dyed	Dyed	Undyed
Time (h)	Pressure (lb/in²)	Excess Taninol WR	Excess Taninol WR	Normal Taninol WR	Undyed only	Dyed only	Normal tannic acid	Excess tannic acid	Excess tannic acid
				Tensile strength (*kg*)					
Not heat-set		27·7	30·1	29·9	30·0	31·8	28·2	31·5	27·7
0·5	15	26·1	24·9	30·0	29·3	32·1	27·5	25·4	25·6
1	15	24·6	22·7	28·8	29·0	31·8	26·3	21·9	22·5
2	15	22·6	19·0	27·4	29·2	30·5	24·3	17·7	15·4

TABLE 12—cont.

Tensile Strengh of Steam-set Nylon 6

Steam-setting conditions		Undyed	Dyed	Dyed	Undyed	Dyed	Dyed	Dyed	Undyed
Time (h)	Pressure (lb/in²)	Excess Taninol WR	Excess Taninol WR	Normal Taninol WR	Undyed only	Dyed only	Normal tannic acid	Excess tannic acid	Excess tannic acid
Not heat-set				*Tensile strengh (kg)*					
3	15	22·1	17·5	23·6	29·4	30·3	21·8	14·2	15·0
0·5	20	23·5	23·4	29·4	29·8	31·6	26·2	21·0	22·6
1	20	21·9	21·8	26·5	29·8	31·1	23·9	16·3	15·1
2	20	21·2	18·4	24·7	28·2	30·7	22·7	10·7	11·0
3	20	18·6	14·5	23·2	27·7	29·4	19·2	7·8	10·4
0·5	25	21·7	15·2	23·5	28·9	30·9	24·6	14·8	20·9
1	25	19·0	14·7	22·8	28·1	30·0	21·1	10·8	12·7
2	25	17·3	14·0	22·3	28·9	29·2	19·5	9·6	9·2
3	25	15·4	11·3	20·1	26·6	28·3	15·1	4·0	5·5
				Loss in tensile strength (%)					
Not heat-set		8*	0*	0*	UC	0*	6*	0*	8*
0·5	15	6	17	0	2	0	2	19	8
1	15	11	25	4	3	0	7	30	19
2	15	18	37	8	3	4	14	44	44
3	15	20	42	21	2	5	23	55	46
0·5	20	15	22	2	1	1	7	33	18
1	20	21	28	11	1	2	15	48	45
2	20	24	39	17	6	4	20	66	60
3	20	33	52	22	8	8	32	75	62
0·5	25	22	49	21	4	3	13	53	25
1	25	31	51	24	6	6	25	66	54
2	25	38	54	25	4	8	31	70	67
3	25	44	62	33	11	12	46	87	80

*Based on untreated control (UC). Other losses are based on the appropriate unset control

RELATION BETWEEN YELLOWING AND LOSS IN STRENGTH

The loss in strength of dyed and undyed nylon 6 or nylon 6.6 increased most rapidly in the early stages of dry-heat setting. The presence of the regain moisture probably led to a high rate of hydrolysis, which decreased as the water was removed. Strength losses were slight, even during prolonged steam setting, and increased at a steady low rate under these conditions. These types of behaviour contrasted with the rate of yellowing of undyed nylon during setting, which increased progressively with time of setting as the concentration of ammonia released by hydrolysis increased and pyrrole formation was increasingly favoured. The loss in strength of backtanned nylon, especially when excess of the tannin was present, was particularly rapid in the early stages of treatment either in hot air or in steam, suggesting that the tanning agent or its decomposition products can catalyse breakdown of the nylon by hydrolysis or oxidation reactions. The yellowing of backtanned nylon was almost entirely attributable to decomposition of the tanning agent to give yellow degradation products, some of which were already present before the setting treatment. Yellowing of the tanning agents increased steadily with time of treatment and was more rapid for the natural tannin than for the syntan treatment. The rate of decomposition of the tannin was higher with nylon 6.6 than with nylon 6, which did not take up so much of the agent initially, and was very much higher in hot air than in steam, where oxidation was minimised.

RELATION BETWEEN LOSS IN WET FASTNESS AND LOSS IN STRENGTH

There was close similarity in the effect of the time of setting on the loss in wet fastness and the loss in tensile strength of dyed and backtanned nylon 6 or nylon 6.6. This was particularly evident under steam-setting conditions, where much of the loss appeared to occur in the early stages of treatment and there was a marked reduction in the rates of loss in wet fastness and tensile strength as setting proceeded. It was also significant that the losses in wet fastness and tensile strength were similar for the samples treated with either the normal or the excessive amount of the syntan, but the excessive amounts in the tannic acid and tartar emetic treatment resulted in much higher losses of fastness and strength than the normal treatment based on the natural tannin. It may be concluded that there is a fairly high degree of correlation between wet fastness and degradation of the nylon as determined by strength loss.

Conclusions

The wet fastness of dyed nylon fibres decreases by about half a point during dry-heat setting for 1–2 min at about 200°C. This is attributed mainly to oxidative degradation of the fibre, which results in a strength loss of 30–40% and considerable yellowing. The wet fastness and strength of dyed nylon fibres slowly decrease during prolonged steam setting, but several hours of treatment at 20–25 lb/in² are required to obtain the effects obtained by treatment for a minute or two in hot air. The yellowing of the fibre during steam setting is very slight, even on prolonged treatment. The decrease in wet fastness of backtanned nylon during dry-heat or steam setting occurs mainly in the early stages of treatment, especially with those samples treated with excess of the agent. The improvement in wet fastness on application of tanning agents to dyed nylon 6 is less than that obtained with nylon 6.6 because less of the agent is taken up by nylon 6. However, the wet fastness of the aftertreated nylon 6 decreases more rapidly during setting because this fibre is more prone to thermal degradation.

The most important causes of the loss in wet fastness of backtanned dyeings of acid dyes on nylon fibres during post-setting treatments are:

(*a*) Thermal oxidation (both types of agent) and hydrolysis (tannic acid only) of the backtanning agent. This cause is the most important for either method of backtanning, but apparently the natural tannin is degraded more rapidly during setting.

(*b*) Thermal oxidation and hydrolysis of the nylon. These processes occur in the presence or absence of a backtanning agent, but are slow in its absence, particularly during steam setting. Hydrolysis is more important in the early stages of dry-heat setting, when the regain moisture is being removed, but oxidation becomes much more important later. Nylon 6 is more prone to thermal degradation than nylon 6.6 and takes up less backtanning agent, so this cause is more important for nylon 6.

(*c*) Catalysis of oxidative or hydrolytic degradation of the nylon by the tanning agent or its decomposition products. This cause is more important for the natural tanning process than for the syntan treatment and contributes more to the loss in wet fastness on steam setting than to that in dry-heat setting.

* * *

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References

1 Peters and White, J.S.D.C., **77** (1961) 601.
2 Sandeman and Keller, *J. Polymer Sci.*, **19** (1956) 401.
3 Black and Doyle, *ibid.*, **3** (1948) 358.
4 Speakman and Saville, *J. Textile Inst.*, **37** (1946) P271.
5 Jeffries, *ibid.*, **51** (1960) T441.
6 Mecklenburgh, Shaw and Peters, J.S.D.C., **68** (1952) 381.
7 Statton, *Symposium on Setting, Manchester* (Jan 1970).
8 McLaren and Rowen, *J. Polymer Sci.*, **7** (1951) 289.
9 Forward and Palmer, *J. Textile Inst.*, **45** (1954) T510.
10 Shore, J.S.D.C., **87** (Jan 1971) 3.
11 Rau and Schwair, *Melliand Textilber.*, **47** (1966) 1423.
12 Truslow, *Amer. Dyestuff Rep.*, **47** (1958) 853.
13 Yasuda and Sato, *J. Soc. Textile Cellulose Ind. Japan*, **13** (1957) 338.
14 Shimizu and Miyaoka, *ibid.*, **14** (1958) 563, 637.
15 Tsuruta, Koshimo and Maehara, *ibid.*, **16** (1960) 215.
16 Agster, *Melliand Textilber.*, **37** (1956) 1338.
17 d'Albignac, J.S.D.C., **82** (1966) 339.
18 Rahman and Farrouq, *Naturwiss.*, **40** (1953) 460.
19 Egerton, J.S.D.C., **64** (1948) 336; *J. Textile Inst.*, **39** (1948) T293.
20 Bubser, *Z. ges. Textilind.*, **65** (1963) 108.
21 Weltzien and Cossmann, *Wiss. Runds. der Textilforschungsanstalt Krefeld*, No. 25 (July 1955); No. 30 (Nov 1955).
22 Fester, *Text. Research J.*, **34** (1964) 362; *Z. ges. Textilind.*, **66** (1964) 955.
23 Sharkey and Mochel, *J. Amer. Chem. Soc.*, **81** (1959) 3000.
24 Boasson, Kamerbeck, Algera and Kroes, *Rec. Trav. Chim.*, **81** (1962) 624.
25 Kroes, *ibid.*, **82** (1963) 979.
26 Rochas and Martin, *Bull. Inst. Text. France*, **83** (1959) 41.
27 Marek and Lerch, J.S.D.C., **81** (1965) 481.
28 Vachon, Rebenfeld and Taylor, *Text. Research J.*, **38** (1968) 716.
29 Wille, *Annalen*, **538** (1939) 237.
30 Kuhn and Dury, *ibid.*, **564** (1949) 32; **571** (1951) 44.

Discussion

Mr H. PARTOVI: Can dyed unbacktanned nylon show an increase in washing fastness as a result of dry-heat or steam setting?

Mr SHORE: With the dye used in the work described here – C.I. Acid Blue 25—there was a significant decrease in wet fastness during dry-heat or steam setting. Some other chemically related dyes also show a similar effect to the same or a less extent, but all dyes for nylon do not necessarily behave in this way. The marked degradation of the nylon fibre occurring during dry-heat setting would be expected to affect the retention of most dyes adversely, but the segmental rearrangement of the molecular chains that occurs, particularly during steam setting, could entrap some dye molecules and make them more difficult to remove. However, we have not found any evidence to support this view.

Mr A. K. PURI: The loss in wet fastness of dyed and backtanned nylon as a result of steam or dry-heat setting could be attributed to the rupture of hydrogen bonds between the dye and nylon. The dye used in this work contains several hydrogen-bond-forming groups. Perhaps a dye that contains less hydrogen-bond-forming groups would behave differently.

Mr SHORE: I agree that hydrogen bonds and other forms of dipole–dipole attraction play a significant part in the dye–fibre interaction, and the segmental mobility imparted to the nylon chains during setting would be expected to loosen the bonds of attachment between dye and fibre and between the tanning agent and the fibre. In steam setting in particular, these molecular rearrangements and the ingress of water molecules into the structure must make a very great difference to the existing pattern of hydrogen bonding in the dyed and backtanned fibre. It would certainly be interesting to examine the behaviour of dyes of other types under these conditions so as to assess the influence of the heat-setting treatments on electrostatic forces and nonpolar bonding between dye and fibre. The results demonstrate, however, that the main causes of the decrease in wet fastness of the backtanned dyeings are decomposition of the tanning agent and its accelerating effect on the thermal degradation of the nylon fibre.

Explanatory Paper

The Principles of Colour Television

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The basic principles of colour television are explained.

Introduction

The object of this paper is to describe the technique whereby colour television pictures can be obtained. In principle, this is no different from other types of colour reproduction, e.g. colour photography and colour printing. The real problems are radio-engineering ones, although their practical solution does entail utilisation of certain facts of colour vision and methods derived from theoretical colour physics. Ideal solutions are relatively easy; the question is: 'How far can the ideal solution be modified, to obtain a compromise solution which will yield a satisfactory colour picture by a practical feasible system?'

Compatibility and Bandwidth

Before discussing the principles of colour reproduction in television it is appropriate to discuss two factors—compatibility and bandwidth—which determine the method that can be used.

Compatibility means the ability to receive the colour-television transmission on a conventional black-and-white receiver as a black-and-white picture, indistinguishable, or nearly indistinguishable, in quality from the normal black-and-white transmission. This is obviously important, in view of the large number of black-and-white receivers already in use which could be tuned to a colour transmission.