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Oxidative stabilization of acrylic fibres

Part 5 *The decolouration reaction*

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When acrylic fibres are heat treated for various times at 220 to 250° C, they form dark, insoluble structures of uncertain chemical character which are inert to many strong oxidizing and reducing agents. The heat-treated fibres are, however, rapidly decoloured by warm alkaline hypochlorite solutions. When fibres which have undergone short-time heat treatment are subjected to the hypochlorite, incubation periods are observed before decolouration is noted; and a swollen acrylic network remains after decolouration is complete. The acrylic network is primarily unreacted precursor units save for a small amount of hydrolyzed material. The decoloured reaction is zero order, indicating a reaction at the surface. The rate of the decolouration reaction also increases with increasing duration of the stabilization heat treatment. In fibres which have undergone partial diffusion-controlled stabilization, a dark mantle surrounds a lightly coloured core. The rate of decolouration is unaffected as the decolouration interface passes from the mantle to the core, indicating that the decolouration reaction is not influenced by the occurance of any sequent reactions. The existence of the acrylic residue indicates that the prefatory reactions are continuing in both mantle and core during the course of stabilization. ^{13}C-NMR spectra of the acrylic residue show the same triad methine peak areas as those obtained on the untreated fibre; hence the stereoregularity of the nitrile groups has no influence on the rate of nitrile polymerization. The mechanisms of nitrile initiation and of decolouration are discussed. The residue obtained by sulphuric acid etch is different from that obtained by hypochlorite treatment. These results suggest that during the early-to-intermediate stages of stabilization, the fibre consists of interpenetrating networks of original material, i.e., fibre which has undergone only the prefatory reactions and fibre which has undergone the sequent reactions.

1. Introduction

It has been known for a long time that acrylic fibres can be converted into carbon fibres [1]. The first step in this conversion involves stabilization by heating the polyacrylonitrile (PAN) fibres at 200 to 290° C in air for several hours. The stabilized fibres are then converted into carbon fibres by subsequent thermal treatment under inert conditions. Although the subsequent reaction conditions have some effect on the properties of the final carbon fibres, it is accepted that the initial stabilization step has a more dominant effect on the properties of the product.

Previous papers in this series have addressed various facets of the stabilization process: the kinetics of stabilization, oxygen up-take and a general model of stabilization [2]; the dynamics of stabilization [3]; a new model for the morphological structure of polyacrylonitrile [4]; the moisture up-take of stabilized fibres [5]. The present paper will consider several low-temperature chemical reactions of stabilized acrylic fibres which demonstrate the existence in the fibres of interpenetrating networks of reacted and unreacted material during portions of the stabilization process.

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One phenomenon accompanying the stabilization reaction has been noted for a long time. That is, the colour of the fibre changes from white to yellow, to orange, to brown and finally to black. Many possible mechanisms have been suggested to explain this phenomenon and the related question of how oxygen is incorporated into the fibre during stabilization in air (e.g. [1, 6, 7]). The precise nature of the reactions involved in stabilization and the structure of the stabilized material remain, however, to be elucidated satisfactorily.

Several reasons for this difficulty in characterizing the reactions and structure may be given: First, the stabilized product is insoluble in any known solvent, and hence normal chemical tests cannot be used. Second, the commonly used technique of infra-red (i.r.) absorption for structural characterization (although quite useful for low molecular weight compounds) is not very helpful in analysing the stabilized fibres (the stabilized fibres give broad, intense absorptions which are very difficult to identify unequivocally).

This therefore requires new methods to obtain information about the stabilized fibre. It has been found that a reaction can cause the colour of the black, partially stabilized fibre to change back to light yellow. This reaction, called a decolouration reaction, involves the reaction of the stabilized fibre with warm aqueous alkaline sodium hypochlorite solutions. In addition, treatment of the partially stabilized fibres with hot aqueous sulphuric acid will dissolve portions of the fibre, with the shape of the residuum depending upon the limiting conditions of stabilization. The observations made in studying these reactions are presented in this paper and are used to develop an improved model of stabilization.

2. Experimental procedure

2.1. Materials

2.1.1. Acrylic fibres

Commercially available Courtelle and Orlon fibres were respun by C. B. Brogna and R. Ruleson at Fibre Research Laboratory to eliminate gross variations in spinning conditions [8]. These fibres, as well as other commercial and experimental acrylic fibres used in the present investigation, are described in Table I. The fibres were partially or completely stabilized by heat treatment under a variety of conditions (see Tables II and III).

2.1.2. Decolouration reagent

Commercially available alkaline sodium hypochlorite, Chlorox, was used as-received. The available chlorine was 5.25% by weight, which is equivalent to 0.76 mol l^{-1}. The pH of the solution was 11.4. In addition to sodium hypochlorite, 0.76 M sodium chloride was present [9]. Hypochlorite will disproportionate into chloride and chlorate above room temperature [10] and will decompose in the presence of metal ions to chloride and oxygen [11, 12], with the ionic species present depending on the pH.

In the present work, a large excess of hypochlorite relative to the fibre mass was used for the decolouration reaction. The possible species present in the warm alkaline solutions employed included Na^+, ClO^-, ClO_3^-, OH^- and Cl^-.

2.2. Observation of the decolouration of stabilized fibres

Acrylic fibres given various heat treatments were used as starting materials for qualitative and/or quantitative examination using a variety of techniques. These included:

2.2.1. Direct method observations

A few individual filaments of heat-treated fibres were immersed in a shallow reservoir filled with alkaline hypochlorite solution. The fibres were pinned between two pieces of 50 mesh platinum gauze to discourage fibre movement yet allow adequate diffusion of reactant and observation of the fibres. The reservoir was closed with a cover slip. The reservoir/slide assembly was then placed on a pre-heated microscope hot-stage to raise the temperature rapidly to the test condition. Colour photographs of the decolouration process of an individual filament were taken using transmitted light from a xenon arc lamp.

2.2.2. Indirect method observations

The stabilized fibres were cut into 1 inch long pieces, and about 100 pieces were reacted with 20 ml of reactant in a capped Erlenmeyer flask. The temperature was kept constant using a water or oil bath. Several fibre lengths were removed after selected time periods, rinsed with distilled water and examined through a Zeiss Universal Research Microscope. The diameters of the fibres were either determined indirectly from photomicrographs or directly by means of a Filar eye-piece. In both cases, the diameter of the

TABLE I Acrylic fibres investigated

Fibre type	Abbreviation	Nominal denier* of yarn	Number of filaments	Denier* per filament	Manufacturer	Co-polymer composition
Monsanto experimental fibre	VA-2	1772	1440	1.2	Monsanto, USA	7% vinyl acetate
Respun Orlon 42	O-440	440	200	2.2	Du Pont, USA (FRL Respun)	6% methyl acrylate
Respun Orlon 42	O-300	300	200	1.5	Du Pont, USA (FRL Respun)	6% methyl acrylate
Orlon 43	O43	tow			Du Pont, USA	6% methyl acrylate
Dralon	D	800	380	2.1	Bayer, Germany	Homopolymer
Respun Courtelle	C-805	805	400	2.0	Courtalds, England (FRL Respun)	6% methyl acrylate, 1% itaconic acid
Commercial Courtelle	C-C	tow	—	4.5	Courtalds, England	6% methyl acrylate, 1% itaconic acid
High tenacity Courtelle	CHT	tow	—	1.5	Courtalds, England	6% methyl acrylate, 1% itaconic acid

*Denier = number of grams in nine kilometres.

TABLE II Decolouration rate of CHT fibres prepared and reacted under various conditions

Stabilization atmosphere	Stabilization time and temperature	Decolouration temperature (° C)	Decolouration rate ($\times 10^3 \mu m\ sec^{-1}$)	Decolouration time (sec)	Decolouration time corrected to 50° C (sec)	Change in diameter of residue phase
Air	127 min at 226° C	50	− 6.0	2900	2900	+ 26%
Air	185 min at 226° C	50	− 12.0	1490	1490	− 34%
		21	− 5.5	3340		− 21%
		65	—	520		dissolves
Air	562 min at 226°C	50	− 22.0	600	600	dissolves
		21	—	5220		+ 49%
Air	4300 min at 226° C	21 (12.5% solution)	—	1400	20*	dissolve
Air	4300 min at 226° C followed by	80	—	6300	5×10^4	dissolves
Argon	660 min at 400° C					
Argon	127 min at 226° C	50	− 6.7	2820	2820	+ 28%
Argon	562 min at 226° C	50	—	1520	1520	+ 12%
Air	25 min at 240° C	50	− 4.3	4500	4500	+ 21%
Air	50 min at 240° C	50	− 6.6	2040	2040	+ 34%

*Corrected for low reagent concentration.

coloured zone and the decoloured zone were noted.

2.2.3. *Infra-red spectroscopy*

KBr discs of processed fibres were prepared by standard methods. Only the occurrence and location of certain bands are reported here because the spectra were quite similar to those already published, e.g. [7, 13–16].

2.2.4. *Proton nuclear magnetic resonance (H-NMR)*

Approximately 40 mg of sample was mixed with 0.5 ml deuterated dimethylsulphoxide (DMSO-d_6) and allowed to stand for several days to effect dissolution without application of heat. A small quantity of insoluble material was removed prior to examination with a Varian T-60 NMR spectrometer.

2.2.5. *^{13}C-nuclear magnetic resonance (C-NMR)*

Approximately 100 mg of sample was mixed with 3 ml of DMSO-d_6 and allowed to stand for several days. The filtered material was examined at 100° C with a Bruker 250 MHz spectrometer.

2.2.6. *Energy dispersive X-ray analysis*

C-805 fibres were pyrolyzed in air at 225° C for 180 min, decoloured in the hypochlorite solution for various times at 40° C in an unstirred solution to prevent removal of the residue phase. The fibres were mounted in a polyester potting compound and polished with 60, 320 and 600 grit sand paper then Al_2O_3 polishing compound. The samples were coated with gold to reduce charging and examined in a Cambridge Stereoscan scanning electron microscope with a KEVEX attachment for energy dispersive chemical analysis. This

TABLE III Correlation between decolouration and stabilization times under various conditions for CHT yarns, $t_{dec} = a(t_{stab})^b$

Temperature (° C)	Atmosphere	a (sec^{1-b})	b	Remarks
226	Air	2.0×10^7	− 1.0	3 points, direct measurement
226	Air	7.4×10^8	− 1.4	4th point corrected, see text
226	Argon	1.2×10^5	− 0.4	2 points only
240	Air	1.9×10^7	− 1.1	2 points only
240	Air	(6.2×10^6)	(− 1.0)	a calculated with $b = -1.0$

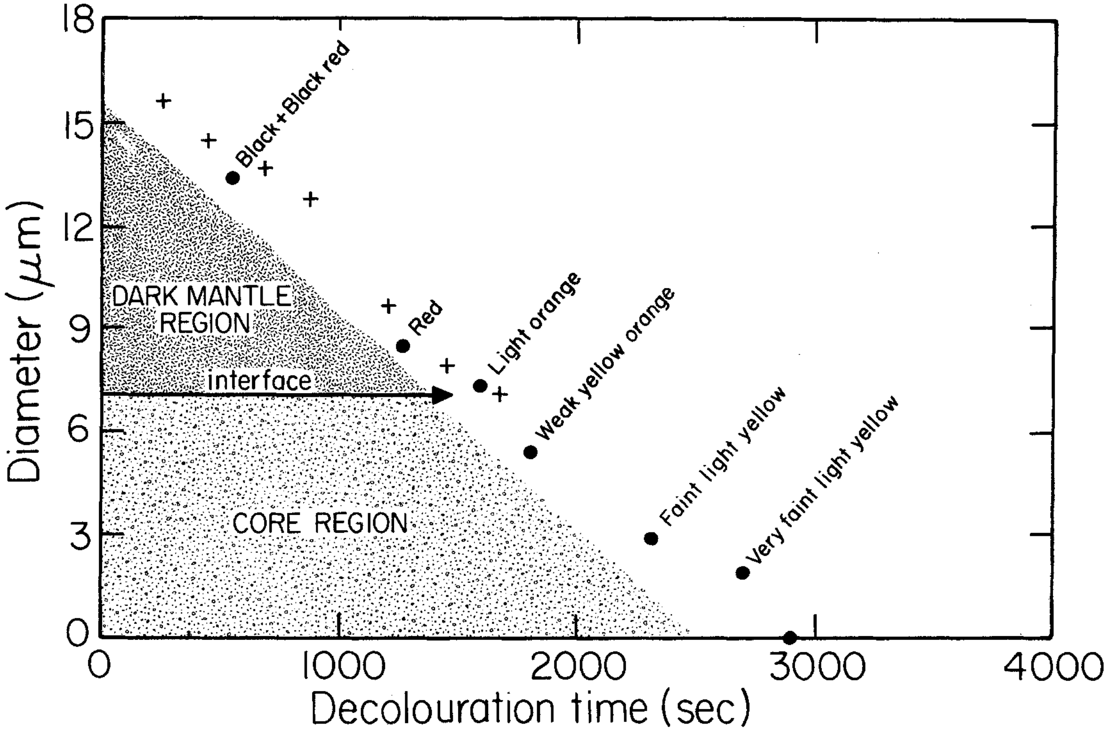

Figure 1 Variation of diameter and colour of CHT fibre stabilized in air at 226° C for 127 min, as a function of time in decolouration reagent at 50° C. The dark mantle and core regions of the fibre prior to decolouration are indicated. The colour notations are only subjective remarks. (●) photographic readings, (+) Filar eye-piece readings.

device was used to measure the radial variations in the concentration of chlorine atoms across the fibre. The accumulated intensity over 60 sec was taken as proportional to chlorine concentration at each location.

3. Results

3.1. Direct observation of the decolouration of individual filaments

When a single filament of C-type yarn (such as CHT) which had been stabilized at 226° C was immersed in hypochlorite solution at 50° C, two types of behaviour were observed. The first, termed Type I, was observed for CHT* fibres stabilized for 127 min. Following an incubation time, an optically-distinct clear zone was seen around the perimeter of the fibre; this clear zone subsequently increased in size at the expense of the central coloured zone. As illustrated by the data in Fig. 1, the diameter of the coloured zone decreased linearly with increasing decolouration time. A representative black and white photomicrograph of such a fibre in the partially-decoloured state is shown in Fig. 2. An inner coloured zone was seen surrounded by an outer swollen, clear or pale yellow residue. The perceived colour of the central phase changed with time as indicated in Fig. 1.

With increasing time of stabilization and the same decolouration conditions, the fibres were observed to decolour at a faster rate, and the amount of clear residue following decolouration decreased. After long stabilization times, the colour of the central phase also changed after decolouration, but no residue was observed. This was termed Type II behaviour.

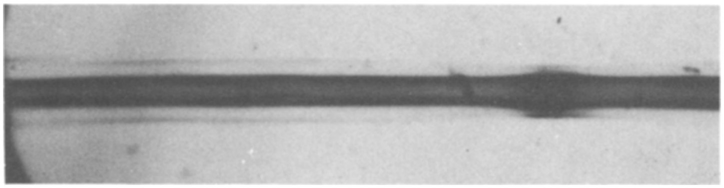

Figure 2 Photomicrograph of CHT fibre of Fig. 1, subjected to decolouration for 26.5 min.

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*For abbreviations see Table I.

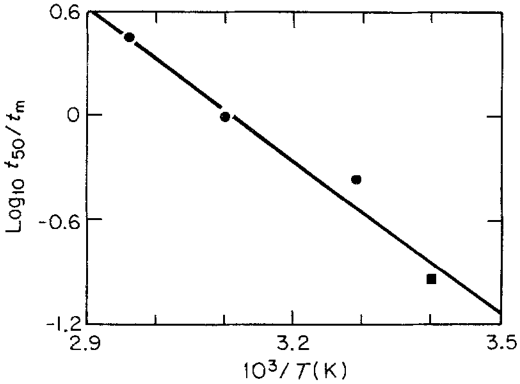


Figure 3 Logarithm of the ratio (decolouration time at 50° C/decolouration time at temperature) against reciprocal temperature for CHT fibre stabilized at 226° C for 127 or 185 min and 562 min (■). The activation energy is 5.8 kcal mol^{-1}.

Although direct observation of the decolouration of individual filaments appeared to be fairly straightforward, the technique presented a number of difficulties. The fibres tended to break up in the later stages of decolouration; the fibres tended to move about in the field of view throughout the reaction; and bubbles (which may be decolouration reaction products, hypochlorite decomposition product(s) or water vapour) accumulated on the fibres and under the cover slip as decolouration proceeded. In many runs, these phenomena prevented adjustments of focus for photography or direct measurements of diameter; and it was only possible to determine the time required for complete disappearance of the coloured phase. In a few cases, these problems did not occur and it was possible to follow the course of the decolouration reaction throughout the entire regime (as shown in Fig. 1 and reported in Table II).

As indicated above, the kinetics of the decolouration reaction were characterized by an incubation period followed by a steady decrease in the diameter of the coloured phase. The time at which the diameter of the coloured phase extrapolates to zero thickness was taken as the decolouration time. The reciprocal of the decolourtion time was proportional to the reaction rate (diameter $= a - kt$, $t_{\text{dec}} = a/k$) (a and k = constants, t = time and t_{dec} = decolouration time). The logarithm of the decolouration time at other temperatures relative to that at 50° C was plotted against $1/T$ in Fig. 3 (T = temperature). From the slope of the line, an activation energy of about 6 kcal mol^{-1} was obtained.

The temperature of the decolouration reaction also influenced the quantity of residue remaining after completion of the reaction: more residue remained at lower temperatures, and at sufficiently high decolouration temperatures, no residue remained. The existence of residue phase also depended upon the degree of agitation of the fibre–reactant mixture. The residue phase was rather fragile and was removed from the fibre if the mixture was stirred during the decolouration reaction.

For lightly stabilized fibres (e.g. 127 min at 226° C), the diameter of the residue phase after decolouration was larger than the diameter of the fibre before decolouration (by about 25% in a typical case). That is, the residue phase was swollen by the reactant solution. For longer stabilization times (e.g. 185 min at 226° C), the diameter of the residue phase was less than that of the initial coloured fibre (by 34% in a typical case). At still longer times (more than 212 min at 226° C), no residue phase remained after decolouration.

The residue phase apparently presented no significant barrier either to diffusion of the reacting species to the reaction front or of reacted species (if any) from the front: a linear decrease in the diameter of the coloured phase was observed whether or not the residue phase was present. Furthermore, there was no detectable optical orientation anywhere in the residue phase; the bi-refringence of the coloured phase was completely destroyed by passage of the reaction front.

Fibres which yielded a residue phase developed cracks during the course of decolouration at 50° C. These cracks appeared towards the end of the reaction and tended to cause the fibre to break up into small pieces or chaff. The crack formation observed took place under much milder conditions than the cracking observed when non-stabilized acrylic fibres were subjected to boiling alkaline hypochlorite solutions [17].

The rate of decolouration increased with increasing stabilization time. Indeed, the fibre reacted for 4300 min at 226° C had to be examined at 21° C in a 12.5% solution of hypochlorite in order to obtain a measurable rate of decolouration. The measured decolouration time for this sample can be adjusted for comparison with other measurements using the kinetic data in Fig. 3 with a direct, but untested, correlation between decolouration time and hypochlorite concentration. In Fig. 4, the logarithm of the decolour-

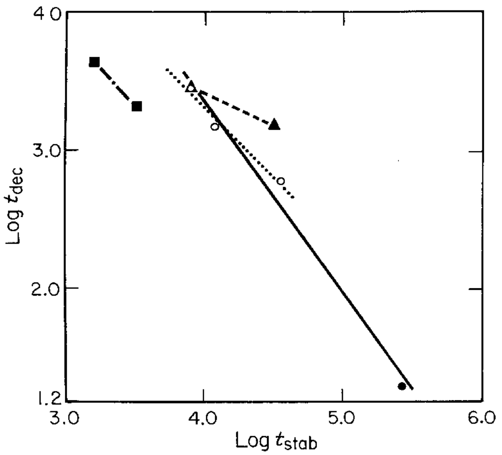


Figure 4 Logarithm of decolouration time at 50° C against logarithm of stabilization time for CHT fibres stabilized in air at 226° C for 127, 185 and 562 min (○) and 4300 min (●) then "corrected" to 50° C (see text); in air at 240° C (■) and in argon at 226° C (▲).

ation time, t_{dec}, is plotted against the logarithm of the stabilization time, t_{stab}, for a variety of conditions. Equations for the straight lines are presented in Table III. The parameters for 226° C in air were estimated by least-squares fit procedures whereas those for 226° C in argon and 240° C in air are based on only two data points.

The species which were formed during stabilization reacted very rapidly with the hypochlorite solution. The higher the concentration of these species, the more rapid the decolouration rate. High temperature treatment, near the upper end of the stabilizaton range, tended to decrease the rate of decolouration: See, for example, in Table II, the CHT fibre treated for 4300 min at 226° C followed by heat treatment in argon for 660 min at 400° C, which decoloured quite slowly, although the fibre did completely dissolve. Perhaps this fibre had already undergone some small amount of heteroatom release or carbonization. Fibres that have undergone extensive carbonization and high-temperature heat-treatment were not decolourized by the hypochlorite solution. Indeed, warm alkaline hypochlorite solutions can be used to oxidize the outer surface of carbon fibres to improve the interlaminar shear strength in composites [18].

Short-time exposure of the same fibres in argon at 226° C gave essentially the same decolouration rate as those treated in air, which suggests that atmosphere does not play an important part in the early stage formation of the groups which are susceptible to hypochlorite attack. Prolonged treatment at the same temperature showed a pronounced effect of atmosphere, with the air-treated fibres decolouring much more rapidly than fibres treated in argon (see Table II).

The CHT fibres considered in Table II contain a weak acid co-monomer, which serves as a catalyst for increasing the rate of stabilization, e.g. [8]. For such fibres, the initial rate of the prefatory reactions should not require the presence of oxygen; and hence the rate of decolouration for short heat treatment times should not depend on atmosphere. As the catalyst co-monomer is used up, initiating the prefatory reactions, the effect of oxygen in catalysing these reactions should become significant; and the extent of the prefatory reactions (and hence the rate of decolouration in hypochlorite solutions) should show a dependence on atmosphere.

3.2. Indirect method of observing decolouration of fibre materials and individual filaments

To obtain rapid results for a variety of stabilization conditions and fibre types, an indirect method of observation was used. Fibres were reacted with warm hypochlorite solution; a small sample was removed and rinsed; and the diameter of the whole fibre, coloured phase plus residue phase, *a*, and the diameter of the coloured phase, *b*, were determined with a Filar eye-piece. A plot of *b*/*a* against time is shown in Fig. 5 for C-805 fibres. Although considerable scatter is observed, a distinct incubation period is noted, and the ratio *b*/*a* is seen to decrease with increasing time.

The scatter in *b*/*a* against time may be associated with variation in the initial fibre (due to the fibre formation process) with variation in stabilization conditions (such as inside against outside filaments in the yarn bundle), or with uncontrolled variations in the decolouration reaction. Even more scatter was observed in plots of *a* against time and *b* against time than in *b*/*a* against time, which suggests the presence of significant variability in the original fibres.

Similar experiments were conducted on C–C fibres (the precursor material for the respun C-805 fibres) which had been treated at 225° C for 210 min. In this case, Type II behaviour was observed; i.e. no residue phase remained after decolouration. A plot similar to Fig. 5 was obtained, except that no induction period was

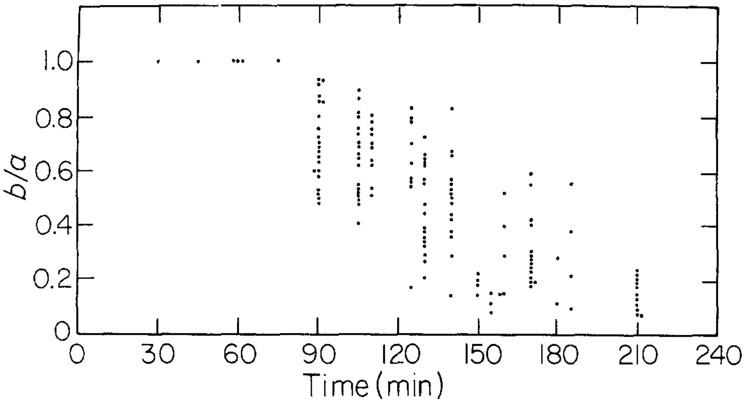


Figure 5 Ratio of coloured phase diameter (b) to residue phase diameter (a) of C-805 225° C as a function of decolouration time at 37.8° C. The variability at any selected time includes data taken along the length of a given fibre and between individual fibres.

noted. During the course of the reaction, the fibre became quite fragile and could not easily be removed from the reaction bath without disintegrating.

The C–C fibres stabilized under milder conditions, e.g. 100 min at 205° C, exhibited Type I behaviour; the parameter b/a again decreased with time, but less scatter was observed relative to that seen in the data for C-805 fibres. The last finding suggests that some of the scatter in the last data may be associated with the respining conditions.

During the course of these experiments, it was noted that for fibres which exhibited Type I behaviour, the colour of the supernatant hypochlorite liquid and the fibre remained unchanged for a period of time, after which the fibre started to decolour. No obvious change occurred in the supernatant liquid or in the size of the fibre. For fibres which exhibit Type II behaviour, the colour of the supernatant phase became non-uniformly deeper and the fibres tended to break into small pieces. The fibres became uniformly lighter in colour and the fibre diameter decreased. Prior to complete dissolution of the fibre, the supernatant phase became less coloured and the pieces of the fibres were quite difficult to see.

In both cases, it was easy to distinguish a time after mixing the fibre and hypochlorite solution when a discernable shift in colour of the fibres occurred. Lightly stabilized, transparent orange to brown coloured fibres also showed a distinct time to affect a colour change or lightening, but no residue phase was detected. Microscopic observation of opaque black fibres showed no colour change prior to a shift in colour from black to brown called t_1. Following this time, red striations appeared which seemed to correspond to the crenulations on the fibre surface. The outer edges of the fibres became more diffuse during this period, but a distinct change in diameter of the coloured phase could not be determined. Fig. 6 shows the time required for an initial colour change as a function of stabilization time at 225° C for both C and O fibres. Both Type I and Type II behaviours are represented in the figure. The induction period measured by this technique (for the first observable change in colour) was far shorter than that detemined for the initial formation of a clear outer zone: a change in the colour of the fibres was noted after only 20 min for C-805 fibres stabilized for 180 min at 225° C (Fig. 6), whereas the residue phase (clear outer zone) was first noted after about 90 min (Fig. 5).

Although the observations detailed in Figs 1 to 5 and Table II were made on C-type fibres, i.e. fibres which contain itaconic acid and undergo a diffusion-controlled mechanism of stabilization at 225° C; similar observations have been made on all the fibres listed in Table I, with Type I behaviour observed for lightly stabilized fibres and Type II behaviour for more stabilized fibres.

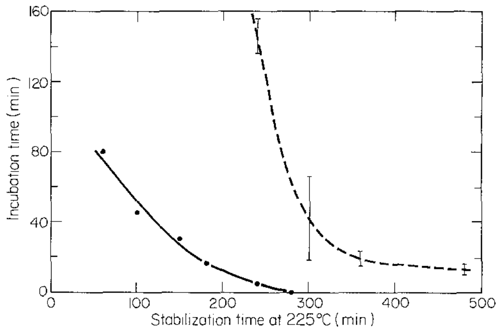


Figure 6 Incubation time, t_1, to the first apparent colour change of fibre mat in decolouration reagent at 40° C without stirring as a function of stabilization time in air at 225° C. Lower curve C-805 fibre. Upper curve, O-42.

The induction periods for fibres which undergo reaction-controlled stabilization are considerably longer than those for fibres undergoing diffusion-controlled stabilization, and the scatter in the data is far greater.

3.3. Analysis of decolouration reaction products

To obtain information on the decolouration reaction products, C-805 fibres heated for 180 min at 225° C were subjected to the decolouration reaction at 50° C with stirring. The colour of the solution rapidly changed from light yellow to brown in about 5 min; the colour of the fibres changed from black to brown. After about 1 h, the colour of the mixture became light yellow, but many fibres could readily be seen. The colour then changed gradually to golden and the fibres were more difficult to see. The pH of the mixture gradually decreased during the course of the reaction, indicating the production of acid material.

After filtration, the filtrate was light yellow. This indicated that the deep colour of the mixture at the later stages of reaction was caused by the suspended coloured fibres. The weight of residue was about 35% of the initial weight of the stabilized fibre. After 7 h reaction, the final solution colour was yellow, the pH was 7.6, and the yield of residue phase was 9% of the initial fibre weight.

The residue phase obtained after 1 h reaction was soluble in dimethyl formamide (DMF) and dimethyl sulphoxide (DMSO); H-NMR and ^{13}C-MNR as well as i.r. spectra were obtained. The solid residue material did not melt when heated to 220° C, but it turned black at about 140° C. The intrinsic viscosity, $[\eta]$, of the residue phase in DMF at 20° C is 0.32 which gives an estimated viscosity average molecular weight, M_v, of 15 000 [19]). The original fibre had $[\eta] = 2.19$ or $M_v = 175000$.

Differential scanning calorimetry (DSC) was also carried out on the residue phase. Although the i.r. and NMR spectra show that nitrile groups are present, a distinct exotherm was not observed upon heating. Rather, a general very broad, slightly exothermic deviation from the baseline was observed.

The filtrate remaining after removal of the residue phase produced a yellow-green precipitate upon acidification with HCl, with a yield of 13.6 to 15.5% of the original weight of black fibre. The acid precipitate was soluble in DMSO and DMF. Extraction of the acidified filtrate by ethyl ether or ethyl acetate produced no organic soluble residue. The acidic precipitate did not melt, turned black at about 140° C and exhibited an uninteresting DSC scan. The η_{sp}–c plot showed the presence of a polyelectrolyte effect. The estimated intrinsic viscosity and molecular weights are 0.27 and 12 000, respectively.

The H-NMR spectra of the untreated C-805 fibres showed four peaks in addition to the DMSO peak. The chemical shifts on the δ scale were approximately (a) 2.0; (b) 3.1; (c) 3.3; and (d) 3.6 ppm. The relative peak area ratios obtained by integration were 2 : 1 : 1 : trace. The first two peaks are therefore associated with (a) $-CH_2-$ and (b) $-CHR-$ protons for the structure $-(CH_2CHR)-$, where R represents nitrile or methyl acrylate groups. Peak c may be due to the presence of small amounts of water, since the hydrogen bonding between water and DMSO will give a characteristic peak at this position [20]. Peak d is associated with the methyl ester protons from the methyl acrylate co-monomer present in the fibre. The identification of the peaks was supported by comparison with the H-NMR spectra of polyacrylonitrile homopolymer and of polyacrylonitrile-co-methyl acrylate (0-440).

The H-NMR spectrum of the residue phase was similar to that of the unreacted C-805 polymer. The peaks at 2.0 and 3.2 ppm (area ratio 2 : 1) indicate that some linear polymer, $-CH_2CHR-$ units still exist. A small peak at 3.4 ppm was difficult to identify, since many types of protons, such as amino, $-H$ in ethers, and $-NCH-$, may be present in this region. The H-NMR spectrum of the acid precipitate also shows the 2.0 and 3.0 ppm peaks (ratio 2 : 1); but the peak at about 3.4 ppm has almost disappeared.

The i.r. spectra of the residue phase is very similar to that of the unreacted polymer, including the characteristic 2240 cm^{-1} nitrile peak. Two additional strong bands are present at 1720 and 1620 cm^{-1}. The former is very likely to be a carbonyl or carboxyl oxygen, while the latter is the characteristic infra-red adsorption of degraded acrylic polymers. It could be a mixture of C=C, C=O and C=N stretching bands and primary N–H bending (1650 to 1580 cm^{-1}). A very strong NH band is present at 3450 cm^{-1} coupled with a band of medium intensity at 600 cm^{-1}.

The ^{13}C-NMR spectra of the residue phase

TABLE IVA Viscosity and ^{13}C-NMR triad tacticity of original and reacted polymers

Parameter	C805 Virgin fibre	Residue phase	Acidic precipitate
M_v	175×10^3	15×10^3	12×10^3
iso	26.2%	23.9%	27.1%
hetero	47.8%	45.3%	44.8%
syndio	26.0%	30.8%	28.1%

TABLE IVB

Parameter	HTC Virgin fibre	Phase A	Phase B
M_v	132×10^3	2.6×10^3	4.8×10^3
iso	25.9%	25.2%	24.6%
hetero	49.7%	53.0%	52.6%
syndio	24.5%	21.8%	22.8%

showed a nitrile triad centred at 119.4 ppm (TMS reference) an unresolved methylene band at 32.6 ppm and a methine triad at 27.4, 27.0 and 26.5 ppm which are identical to those in the unreacted polymer. Based on Schaefer's assignments [21] the methine lines are taken as measures of the syndio-, hetero-, and isotactic placements in the polymer, respectively. The relative concentrations of these placements are given in Table IVA and B.

The infra-red spectra of the acid precipitate was almost identical to that of the residue phase. This, coupled with the H-NMR and ^{13}C-NMR spectra indicate that the two materials are very similar and contain unreacted polyacrylonitrile units.

The residue phase collected from CHT fibre stabilized in air for 197 min at 221° C and reacted in hypochlorite solution for 85 min at 45° C was washed and centrifuged. The centrifugate consisted of two sharply demarcated layers. The lower layer, Phase A, (13% yield, based on the weight of the pyrolized fibre) had a light sandy opaque colour when dry. The upper layer, Phase B, (4% yield) had a dark tan translucent colour when dry and was quite brittle. The i.r. spectra were indistinguishable, except that Phase B had slightly more intense peaks in the carboxylic region.

The viscosity average molecular weights were calculated either from a single specific viscosity or from the intrinsic viscosity by means of the Billmeyer and Onyon equations. The results are shown in Table IV. Because the i.r. and NMR spectra show that changes in composition have occurred and there may also have been an alteration in molecular weight distribution through chain scission, the calculated molecular weights for the residue phases may be different from the actual values.

TABLE V Effect of sulphuric acid etching on O-43 fibres heat treated at 225° C in air

Heat treatment (h)	Colour prior to etching	Residue appearance after 2.5 h exposure to aqueous H_2SO_4 under reflux
1	Yellow	Clear gel, very fragile
2	Gold	Clear gel, rough surface
4	Deep brown	Open sponge-like texture, brown
8	Black	More dense spongy texture, black
24	Black	No reaction, intact, black, smooth

The ^{13}C-NMR spectra of Phases A and B were essentially identical to that of the unreacted CHT fibre, save that the very small methyl ester peak (at 52.1 ppm in the unreacted fibre) has disappeared. Also, the nitrile triad is now resolved into its nine constituent pentad peaks. The peak resolution may have been improved by half an order of magnitude due to an increase in relaxation time resulting from a decrease in molecular weight. The methine triad does not show any further splitting in the degraded polymer. The relative areas of the three methine peaks are given in Table IV.

3.4. Sulphuric acid etching

Fibres of essentially identical composition save for the presence or absence of itaconic acid were heat treated for various times at 225° C in air or in nitrogen, and then subjected to a 2.5 h etch in 50 wt% aqueous sulphuric acid under reflux and the residue was examined in the light microscope.

Fibres treated in air which do not contain the weak acid catalyst left a sponge-like residue (Table V). The concentration of solid material in the sponge increased with increasing stabilization time; and after long stabilization times, the fibres were unaffected by the sulphuric acid treatment. The sponge-like material was fragile and could not be manipulated to examine its cross-sectional features. Longitudinal observations gave the impression that the solid was continuous across the entire fibre diameter.

The spongy residue observed in this work should be contrasted with the annulus of material

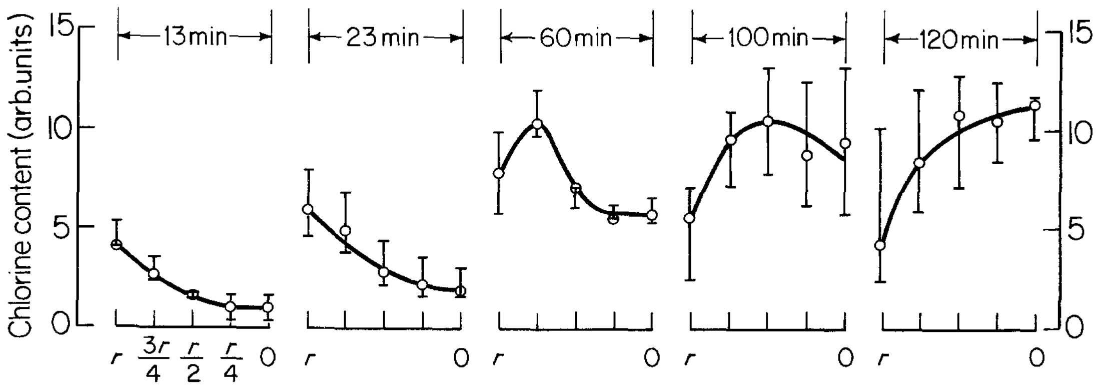


Figure 7 Variation of chlorine concentration across a fibre radius as a function of decolouration time at 40° C for C-805 fibre stabilized for 180 min at 225° C. The circles are based on the "best fit" line when data is plotted as chlorine content against time for each position. For this fibre, $t_1 = 20$ min, $t_2 = 90$ min, r = radius.

which remains after sulphuric acid treatment of fibres containing the catalytic monomer which have been heat-treated in air to form the dark mantle. The annulus residue in the latter case, particularly after intermediate times of stabilization, seems unaffected by sulphuric acid. The dimensions of the annulus correspond closely to the dimensions of the dark mantle in the heat-treated fibres.

3.5. Chemical analysis of cross-sections of fibres exposed to hypochlorite solutions

C-805 fibres stabilized at 225° C in air for 180 min were subjected to hypochlorite solution at 40° C for various times without stirring. At preset times fibres were withdrawn from the decolouration bath and dried without rinsing to minimize alteration of the chlorine content across the fibre. X-ray analysis for chlorine was performed at five positions across a fibre radius, taking care to examine surfaces free of debris. The positions were at the fibre centre and 1/4, 2/4, 3/4 and the edge position of the fibre radius. Four or five individual fibres were examined for each decolouration time. Fig. 7 shows the chlorine concentration across the fibre radius as a function of decolouration time. The error bars are the standard deviation of the measurement. The circles at each position are based on the "best-fit" line when the data was cross-plotted as chlorine content against time for each position. Such plots allowed the origin to become a "sixth" point. Independent tests demonstrated that chlorine species will not penetrate unstabilized fibres under the test conditions.

4. Discussion

4.1. Review of models of stabilization

Previous publications in this series have advanced a model for the stabilization reaction of acrylic fibres. The model as reviewed by Warner *et al.* [2] is as follows. The reactions involved in stabilization, while too complex to specify in detail, can be divided into two categories: those which occur prior to and including nitrile polymerization, called "prefatory reactions", and those which occur subsequent to nitrile polymerization and involve the newly created species, termed "sequent reactions".

Two limiting mechanisms of stabilization were also described, which represent diffusion-controlled and reaction-controlled kinetic processes. In the reaction-controlled process, the overall reaction rate is limited by the prefatory reactions. The sequent reactions occur sequentially and simultaneously with the prefatory reactions. In the diffusion-limited case, prefatory reactions occur relatively rapidly throughout the fibre, due to the presence of catalyst, to preconditioning steps or to the heat transfer capability of the fibre bundle with the ambient atmosphere. The sequent reaction follows more slowly as the diffusion of oxygen to reactive sites is limited by previously oxidized material.

The model further suggests that fibres which undergo reaction-limited stabilization exhibit a uniform darkening of the fibre cross-sections with time and the rate of oxygen up-take is linear with time. In contrast, fibres which undergo diffusion-limited stabilization typically show a two-zone morphology of a lightly coloured core, a deeply coloured outer mantle and a sharp interface between the two zones. Movement of the zone interface towards the fibre centre and oxygen up-take both depend linearly on the square root of time, at least for times greater than some initial time required for establishment of the two-zone morphology.

Fibres which exhibit reaction-limited stabilization are not etched completely by hot aqueous sulphuric acid, nor are the mantle regions of fibres undergoing diffusion-limited stabilization. The light-coloured cores of the latter fibres are, however, completely dissolved by the sulphuric acid treatment [2]. The finding that stabilized fibres are decoloured by alkaline hypochlorite solutions and the further examination of fibres undergoing sulphuric acid etching has led to a number of modifications and refinements of the above model as will become apparent from the ensuing discussion.

4.2. Incubation time and chlorine penetration

The process of the decolouration reaction for lightly stabilized fibre is characterized by two incubation periods. During the first incubation period, no change in the colour of the fibre was noted. Then during a relatively short time interval, beginning approximately at a time designated t_1, a colour change was determined in the fibre–hypochlorite solution mixture. After t_1, small changes in colour were observed but the diameter of the fibre did not change. After the second incubation period, designated t_2, the diameter of the coloured phase decreased linearly with increasing time. The length of the incubation periods t_1 and t_2 and the scatter observed in determining t_1 depended upon the fibre type and the stabilization conditions. Fibres undergoing diffusion-limited stabilization generally show shorter t_1 values and less scatter than fibres undergoing reaction-limited stabilization. With increasing stabilization time the incubation periods decreased and the variation in measured values of t_1 also decreased.

When both incubation periods were observed, then an acrylic network residue phase was also observed whose diameter and density depended upon the stabilization conditions. When the incubation times and the residue phase were not observed, the fibres simply decreased linearly in diameter with reaction time coupled with an apparent colour change.

Prior to the incubation time t_2, chlorine species were observed to diffuse into the fibre interior, with the chlorine profile depending upon the exposure time to decolouration agent. Significant penetration of chlorine species occurred at 13 min even though the first observable colour change occurred at $t_1 = 20$ min. The chlorine content at the outer edge at first increased then later decreased suggesting that some chlorine species are soluble in fibre containing prefatory and sequent groups. The decolouration reactions form species in which the total chlorine solubility is lower. Thus at later stages of decolouration, the chlorine content is greatest in the centre of the fibre. It is anticipated that the chlorine gradient across the fibre would depend not only on the exposure time and temperature of the decolouration reagent but also on the extent of stabilization. The technique used to measure the distribution of chlorine in the fibres cannot distinguish between chloride, hypochlorite or chlorate ions. These ions differ in oxygen content, but the technique cannot measure oxygen concentrations. In any case, the presence of hydrolysis products would render difficult any determination of the ion structure.

The broader variation in measured t_1 values in the reaction-limited case reflects different fibres in the mixture undergoing colour changes at different times. This effect may be the result of inhomogeneities within the individual fibres prior to stabilization or it may be due to inhomogeneous stabilization, perhaps caused by oxygen attacking the outside filaments of the yarn bundle before it attacks the more centrally located filaments.

Both incubation times very likely result from a combination of the denser surface texture of the acrylic filaments, the presence of non-reactive groups initially blocking ingress of the ions into the fibre interior, to the establishment of a boundary layer. Once the residue phase is present, the stresses at the interface due to the swollen phase precludes the blocking action.

4.3. Kinetics of decolouration

The zero-order kinetics, as shown in Figs 1, 3 and 4, and the results given in Table II, relate to the changing diameter of the coloured zone, not to the attack of chromophores. The dissolution of solids into liquids [22] is influenced by processes such as diffusion, concentration gradients, convection, variations in surface energy effects due to variations in radius of curvature, thermal gradients and heat transfer. In the absence of these effects, the process of dissolution should depend only on the concentration of soluble material per unit area exposed to the solvent and the energetics of transfer from the solid to the solution phase [23, 24].

The weight of material dissolved from a fibre (or a long cylinder) in a given time will depend on the surface area, i.e., $2\pi r \mathrm{d}r$ (r = radius); and the diameter of the dissolving cylinder at a given time will depend on the surface concentration of dissolving material. Thus, the rate dependence shown in Fig. 1 is related to the concentration of active material at the surface. Because the diameter of the coloured zone decreases linearly with time, the surface concentration of reactive groups must be independent of radius. Suppose now that the concentration of active material depends on the stabilization time and the active material is reasonably homogeneously dispersed in an inert matrix. As the concentration of active material at the surface increases, and in the absence of complicating factors such as those cited above, the rate of dissolution should increase in proportion.

The action of hypochlorite on a stabilized fibre to produce a swollen decolourized residue phase appears to be a zero-order attack on chromophores at the interface between the coloured phase and the decoloured phase. Although it has already been shown that chlorine species have penetrated to the fibre centre before the decolouration reaction starts, the identity of the ionic species in the fibre centre is not known. Because only hypochlorite ions will cause decolouration, it is assumed, but not demonstrated, that a sharp gradient in hypochlorite ion concentration exists at the decoloured–coloured phase interface. The decrease in diameter, d, of the coloured zone is linear with time and can be represented:

$$d = d_0 - k(t - t_2), \qquad (1)$$

where d_0 is the diameter of the particular fibre investigated; t_2 is the incubation time and k is the kinetic constant represented by the slope of the diameter of coloured zone against time relation. The constant k is proportional to the concentration of active species at the boundary between the coloured and decoloured zone. The time when d goes to zero, t_{dec}, is equal to $(d_0 + kt_2)/k$, i.e. inversely proportional to the rate constant. Because of the difficulties in following the decolouration reaction in a quantitative manner, as noted in Section 3 above, some of the data are reported only as the time for complete decolouration, t_{dec}. Thus the activation energy for the decolouration process obtained from Fig. 3, as well as the effect of stabilization time on decolouration time (Table III), may include a contribution from the $(d_0 + kt_2)$ term if it varied from test to test.

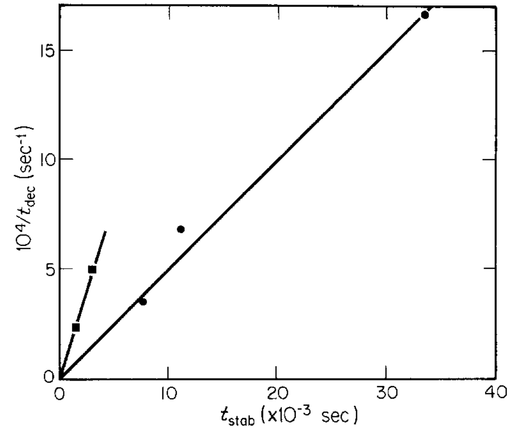


Figure 8 Reciprocal of decolouration time against stabilization times under the assumption that a 1 : 1 correlation exists. (●) 226° C, (■) 240° C. The calculated activation energy is 42 kcal mol^{-1}.

If the data point at 226° C, 4300 min is eliminated because of the uncertain effect of the hypochlorite concentration on decolouration rate, there appears to be a one-to-one inverse relationship between decolouration and stabilization times (Fig. 8). There is insufficient data to test whether or not the correlation exists over sufficient times for fibres with and without the catalytic co-monomer. However, if the correlation is assumed to hold for the CHT type fibre at both 226 and 240° C, then an activation energy of about 42 kcal mol^{-1} is obtained.

One remarkable result of the decolouration studies is that no obvious discontinuity in the rate of decolouration occurs as the diameter of the coloured zone passes from the dark mantle into the lightly coloured case of fibres exhibiting a two-zone morphology. The existence of the residue phase in fibres exhibiting the two-zone morphology indicates that prefatory reactions continue to take place within the dark mantle. Sequent reactions take place in the dark mantle, but not in the lightly coloured core.

The major differences between groups that have undergone prefatory reactions and those that have further undergone sequent reactions, involve the removal of hydrogen and the addition of oxygen. The concentration of nitrogen atoms within prefatory-reacted and sequent-reacted groups should, however, be the same. One explanation for the lack in specificity of hypochlorite reaction with prefatory and sequent groups is that the specific unit being attacked is identical in the two cases. This explanation further requires that the reactivity of the specific unit is unaffected by (a) the presence or absence of oxygen atoms covalently bound to nearby atoms in the polymer chain, and (b) the occurrence or non-occurrence of dehydrogenation or aromatization. These conditions seem reasonable if the rate of reaction with the specific group is sufficiently fast. An alternate explanation is that the prefatory groups are rapidly oxidized by hypochlorite to form sequent groups, which then undergo the decolouration reaction. The conversion of prefatory to sequent groups can also occur during a portion of the incubation period prior to t_2 when the fibre is being penetrated by chlorine-containing species.

Additional evidence for the equivalent reaction rates of prefatory and sequent groups to hypochlorite attack is found by comparing the rate of decolouration of C-type fibres stabilized for 127 min at 226° C in air and in argon. The air-stabilized fibre has a fully developed two-zone morphology, while the argon-stabilized fibre exhibits only a uniform pumpkin-orange colour. Both fibres decolour at essentially the same rate. This is consistent with the model provided the bulk of the prefatory groups have been formed (within the time considered) by the initial content of residual initiators and very few are formed by the results of oxidation in the mantle. Fibres which do not contain the weak acid co-monomer are only lightly coloured and have undergone only a small amount of oxygen up-take when stabilized under these same conditions [2, 8].

Fibres which contain the weak acid co-monomer, heat-treated in air and argon for 562 min at 226° C, both show enhanced rates of decolouration compared with the same fibres treated for shorter periods of time. This indicates that oxygen-initiated and inert-initiated prefatory reactions have occurred. The rate of decolouration of the air-stabilized fibres is, however, about 2.5 times faster than that of the argon-treated fibres.

Given the premise that prefatory- and sequent-reacted groups react at the same rate with hypochlorite solution, the lack of a discontinuity in decolouration rate between the two zones of a fibre stabilized under diffusion-controlled conditions may simply reflect the differences in concentration of prefatory-reacted groups between the two zones being too small to be observed using the present techniques. Specifically, the concentration of prefatory-reacted groups initiated by the co-monomer initiation apparently considerably exceeds the concentration initiated by oxidation products.

4.4. The existence of the residue phase

The existence of the residue phase in lightly stabilized fibres, especially in those displaying diffusion-limited kinetics, demonstrates that the prefatory reactions are not complete prior to the onset of the sequent reactions. Thus, the prefatory reactions are a slow process and still proceed after the dark outer mantle has been formed and is encompassing greater portions of the fibre cross-section. The prefatory reactions involve in part the creation of initiators for nitrile polymerization, the initiation thereof, and nitrile polymerization. The latter reaction produces much heat which must be adequately removed in order to prevent destructure run-away reactions, e.g. the characteristic acrylic exotherm. Therefore, the prefatory reactions must be controlled to avoid the exotherm, yet be fast enough to result in an economical process.

The catalyst content of the C-type fibre, represented by the itaconic acid co-monomer, is only present at an adventitious level. The co-monomer is incorporated into the commercial acrylic yarn in order to improve the basic dye-ability of the textile. For economic reasons, a portion of the production of this acrylic polymer has been diverted to product of carbon fibres. Hence the content of the weak acid co-monomer has very likely not been optimized for the most efficient production of stabilized yarn.

The C-type fibres are apparently wet-spun from an aqueous solution of approximately 50% sodium thiocyanate at a pH of 5.3 to 6.5 into a coagulation bath of approximately 11% sodium thiocyanide, and the resultant fibres may be washed at a pH of 5.7 [25]. At a pH of 5.3, the degree of dissociation is about 69%; at pH = 5.7, about 81%; and at pH = 6.5, about 96%, based on pK_a

values of 3.85 and 5.45 [26]. Thus four different types of initiator groups exist in the co-polymer that contains itaconic acid. These are two non-ionized and two ionized carboxyl groups. The ability of these groups to initiate nitrile polymerization is certainly not identical.

The modest concentration of weak acid co-monomer in the C-type fibres leads to the expectation that they will initiate polymerization of only a portion of the nitrile groups in the fibres. Subsequent initiation of nitrile polymerization (and occurrence of the prefatory reactions more generally) should take place more rapidly in the dark mantle than in the core. Hence, further prefatory and sequent reactions will take place in the mantle while the mantle–core boundary advances towards the centre of the fibre with sequent reactions taking place at the boundary. This effect is expected to produce a pronounced concentration dependence of the oxygen diffusivity in the mantle.

The initiators for nitrile polymerization include three separate forms: those initially present in the fibre before stabilization temperatures are attained [27]; those which are created under inert stabilization conditions; and those which are created under oxidative stabilization conditions [28]. The overall rate of nitrile polymerization is very likely rapid for initiators initially present in the fibres, slow for those which are created by oxidative attack, and very slow for those created under inert conditions.

The attack of warm aqueous sulphuric acid on lightly reacted fibres undergoing diffusion-controlled stabilization is consistent with the prefatory and sequent reactions occurring simultaneously in the dark mantle. Brogna [8] has shown that the core material is completely dissolved away, leaving a thin collapsed ribbon of outer material. The surface topology of the outer material is unchanged from that of the unetched fibre.

The transport of sulphuric acid in such etching apparently takes place through the outer mantle, since the collapsed ribbons show no evidence of etching only from the fibre ends. If the latter process were the primary mechanism, one would expect to see fibres (after recovery and drying) exhibiting collapsed ends and unattacked centres (similar to a straw which has been flattened at the ends).

Fibres stabilized for short times under reaction-controlled conditions exhibit a swollen foam-like residue following sulphuric acid attack. The density of the foam increases with increased stabilization time. The evidence provided by Warner *et al.* [2] was based on fibres stabilized for sufficiently long times that the foam structure after sulphuric acid etching was quite dense.

The structure in these cases, with modest but definite porosity, is at least qualitatively similar to that inferred for the mantles in fibres stabilized under diffusion-controlled conditions. In the latter case, sufficient porosity exists to permit the transport of sulphuric acid to the centres of the fibres. A given stage of development occurs at much earlier times in the mantles of the catalyst-containing fibres than in the volume of fibres without the catalyst.

Based on the evidence that the residue phase is present at early stages of stabilization in fibres which exhibit both diffusion-limited and reaction-limited kinetics, and that the sulphuric acid etch produces a porous structure in both cases, it seems that at least three types of sequences are present in the fibres: unreacted acrylic sequences, those which have undergone only the prefatory reactions, and those which have also undergone the sequent reactions. These sequences must exist as interpenetrating networks. In the swollen state the networks are sufficiently open to allow diffusion of aqueous sulphuric acid through sequent phase to attack the unreacted and prefatory reacted segments and to allow diffusion of hypochlorite solution to attack the prefatory- and sequent-reacted segments.

4.5. Colour changes during decolouration

During the course of the decolouration reaction, the fibres undergo visual colour changes. Quantitative spectra of fibrous material are difficult to obtain, and require a considerable quantity of carefully prepared sample and special equipment to record the reflectance spectra. Quantitative transmisttance spectra on fibre dispersions require special care to maintain homogeneity and correction for the amount of scattered light and other effects.

Such measurements were beyond the scope of this study. Unpublished studies on solutions of acrylic polymer which had undergone various extents of base degradation exhibited various shades of colour from deep brown to light yellow and had attained colour equilibrium, all had identical visible ultra-violet spectra [29]. There were no band shifts towards the visible as a function of colouration reaction. Instead, the existing characteristic ultra-violet bonds merely increased in intensity.

The reported bleaching of these solutions upon addition of acid is incorrect (the solutions were merely diluted, as demonstrated by quantitative spectral studies). Apparently the human eye is quite sensitive to small changes in concentration in the blue–violet region, which appear to the observer as major colour changes. These colour changes cannot be interpreted as significant changes in the molar extinction coefficients. Kubasova *et al.* [30] show ultra-violet spectra of polyacrylonitrile homopolymer prepared either by radical polymerization or in urea canal complexes by γ-irradiation, dissolved in dimethyl formamide, then thermally degraded. Again, there is no obvious shift in band structure towards longer wavelengths, only an intensification of the spectra as a function of degradation time. Similar results have also been obtained by other investigators [31, 32].

The reduction in diameter of the coloured zone can also lead to confusing perception of colour. Because the diameter decreased linearly with time during the decolouration reaction and because no plasticized zone could be discerned ahead of the interface (even though chlorine species were found to have penetrated the interface) it is suggested that the observed colour changes of the central coloured zone are due to changes in the physical size of the coloured zone or by dilution of the fibre chromophores by chlorine atom solution rather than to chemical action taking place within the coloured zone. A discontinuous jump in apparent colour does occur during the decolouration reaction on C-type fibres as the reaction front traverses the original mantle–core interface.

4.6 Fibre cracking and break-up

Fibres pyrolyzed in air at 226° C for short periods of time develop cracks in the residue phase during the course of the colouration reaction. These cracks appear towards the end of the reaction when the dimensions of the coloured core are rather small. The majority of these cracks are longitudinal and extend along the fibre axis for sizeable distances (up to 100 μm). Some circumferential cracks and a few oblique cracks have also been noted. The development of large, wide cracks is more extensive for less stabilized fibres which, according to Table II, yield a residue phase whose diameter exceeds that of the original stabilized fibres. The cracks described here are produced under much milder conditions than the circumferential cracks produced in untreated acrylic fibres exposed to boiling hypochlorite solutions [17]. In isotropic hollow cylinders, the hoop strength is one-half that of the axial strength [33]. Hence the longitudinal cracks are very likely to be caused by the swelling of the residue phase coupled with its fragile character. As noted above, there is no obvious change in length of the fibre with decolouration time for fibres which exhibit Type I behaviour. In contrast, for Type II behaviour the fibre tends to break up into small pieces; and the fibre–reagent mixture appears to become coloured. Upon filtration, a fine coloured chaff is collected along with an essentially colourless filtrate.

4.7. Mechanism of decolouration

It has been seen that stabilized acrylic fibres are rapidly decoloured by warm alkaline hypochlorite solution. The same fibres are *not* decoloured by weak alkaline solutions, alkaline solutions of sodium chloride or sodium chlorate, or by acid solutions of hypochlorous acid. Hence the active species in decolouration must be the hypochlorite ion.

According to Chakrabartty [34] pyridine is a highly oxidative-resistant organic solvent that is also attacked by alkaline hypohalite solutions. These rather mild oxidants rapidly reduce pyridine to ammonia and carbon dioxide. Attempts to characterize the intermediate products by rapid quenching and combined gas chromatography–mass spectroscopy were not successful.

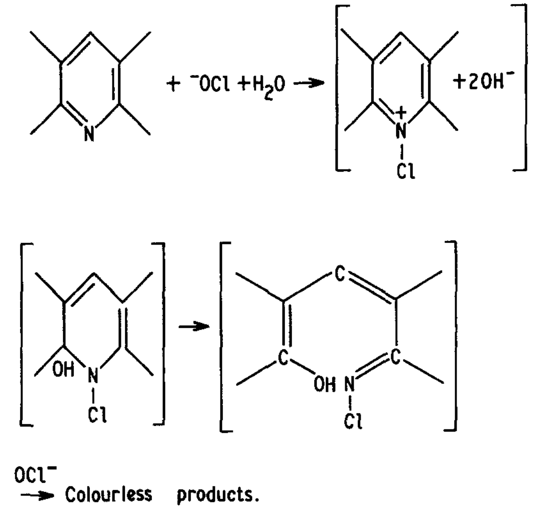
Previous studies [35] showed that polyenes could be distinguised from polyimines by the use of basic hydrogen peroxide, but that stabilized acrylic fibres were not decoloured by this reagent. The stabilized fibre is unaffected by reagents such as strong acids, strong bases, many strong oxidizing agents (perchlorate, peroxide, permanganate, dichromate) and strong reducing agents (various hydrogenation procedures, sodium borohydride, diborane, lithium aluminium hydride). Therefore the structure of the chromophores must be of a type susceptible primarily to hypochlorite attack, such as the nucleophillic pyridine-type structure.

The hypochlorite ion reacts rapidly as an electrophile in the presence of a nucleophile due to the facile cleavage of the O–Cl bond:

$$\text{O–Cl}^- + \text{Nucleophile} + \text{H}_2\text{O} \rightarrow$$

$$2\text{OH}^- + \text{Cl–Nucleophile}. \qquad (2)$$

The activated $\text{Cl–}\overset{+}{\text{N}}\text{ucleophile}$ product can then undergo rapid hydrolysis or other degradative reactions [36, 37]. Thus:



The non-aromatic bonds in the last postulated structure should be rapidly attacked by the hypochlorite ion. If the nitrile group undergoes basic hydrolysis to the amide, the latter should rapidly be reduced to an amine plus CO_2 by the Hoffman reaction.

Polyacrylonitrile is slowly attacked by mild base to undergo prefatory-type reactions with the formation of reddish chromophores. Such reactions should also occur in warm alkaline hypochlorite reagent, but any prefatory products so produced would rapidly undergo the decolouration reaction. Perhaps the gradual disappearance of the residue phase upon prolonged exposure to hypochlorite solution is due to the latter set of actions. In contrast, acetonitrile is one of the few solvents stable to hypochlorite solutions [38].

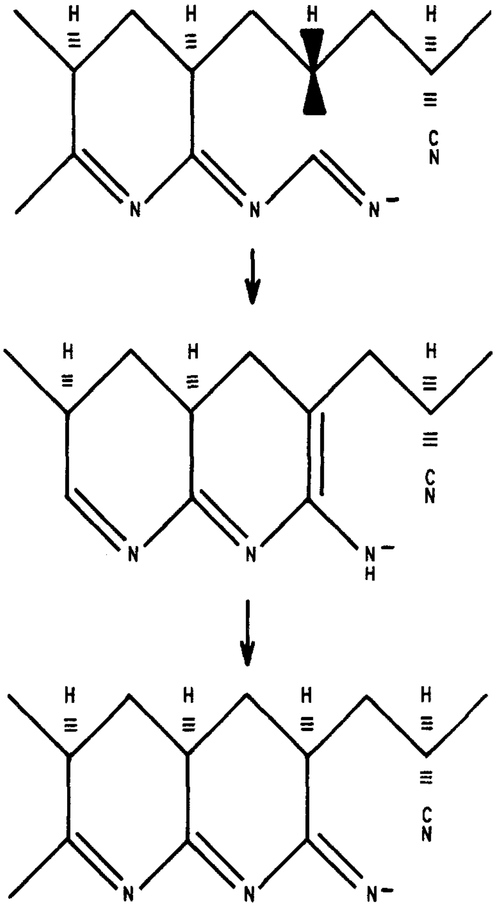
4.8. Nitrile polymerization and stereoregularity

Examination of Table IV shows that the methine tacticity of the original polymer is essentially identical to that of the residue phases collected after stabilization and decolouration. This information can be used to elucidate the microstructure of the fibres and how the microstructure influences the nitrile polymerization reaction. Thus, in a purely heterotactic polymer, some 12.5% of the polymer must be in syndiotactic sequences equal to or greater than three units in length; and a similar amount must be in isotactic sequences equal to or greater than three units in length. Thus, if there is a greater tendency for isotactic units to be incorporated into the polymerized nitrile chain, there should be an enrichment of syndiotacticity in the residue phase. Since this was not observed, then syndiotactically placed nitrile groups must have equivalent reacticity with isotactically placed groups.

This conclusion is not in accord with other work in the literature, which examined the thermal stability (considered equivalent to nitrile polymerizability) of PAN homopolymers prepared under conditions expected to enhance the isotactic content of the polymer. Dinh *et al.* [39, 40], Kubasova *et al.* [30] and Geiderikh *et al.* [41] studied polymers of enhanced isotactic content, prepared using urea-canal complexes. They found that the isotactic-rich polymers enhanced the rate of colour formation, have a higher concentration of paramagnetic centres, and suffer less weight loss than more normal free radical polymerized material: while the polymer prepared in the urea-canal complexes exhibited enhanced reactivity and enhanced isotactic content, it was not established that the two materials tested had approximately the same initiator content. Furthermore Minagawa and Iwamatsu [27] show that the free radical polymerization recipe can have a marked influence on the peak temperature of the nitrile polymerization exotherm which is due to variations in polymer uniformity.

Some authors claim that syndiotactically placed nitrile groups cannot be incorporated into a polymerized chain because studies with molecular models indicate a high degree of strain [30, 39, 40]. It should be noted, however, that cyclobutane and cyclopropane cannot be formed with some models. Further, space-filling molecular models and skeletal Dreiding models allow long sequences of synodiotactic acrylonitrile units to become cyclic without appreciable strain on the bond angles.

A more realistic explanation for the lack of stereospecificity may be obtained by invoking a rapid imine–enamine tautomerism of the ultimate cyclicized nitrile unit which will cause racemization or scrambling of any possible chiral centres. That is:



These scrambling reactions may be quite rapid at 200 to 300° C. Thus, attempts to improve the rate of stabilization by altering the tacticity of the original polymer would probably not be fruitful.

The precise structures of the residue and acid precipitate polymers have not been determined. Although the polymers so far characterized contain roughly 50 to 250 repeat units, the relative concentrations of nitrile, acid, ester and amine units (among others) are not known. If these polymers contain up to 80 to 85% acrylonitrile, then the *average* run length would be about four acrylonitrile units. Cook [42] showed that model oligomers of polyacrylonitrile up to the tetramer did not exhibit a sharp exothermic reaction. Neither do the residue or acid precipitate polymers thus far tested. The minimum chain length necessary to cause the violent exothermic reaction has not yet been established. The acid precipitate is very likely the acrylic residue which has undergone slow attack by the basic hypochlorite solution. Although the acid material does contain an enhanced concentration of carboxylate groups, they do not predominate as the material is soluble in DMSO whereas polyacrylic acid is not.

5. Conclusions

(1) Alkaline hypochlorite solutions will decolourize partly or fully stabilized acrylic fibres. The decolouration process for lightly stabilized fibres occurs in two distinct steps. After an incubation period, t_1, the fibres exhibit a lightening in colour as chlorine-containing species diffuse throughout the fibre, but the fibre remains coloured. After a further incubation time, t_2, the coloured zone starts to decrease in diameter. The decrease in diameter of the coloured zone is linear with decolouration time. Such zero-order kinetics are similar to those observed for the dissolution of a solid under reaction or convection control. For fibres that have been more extensively stabilized, two distinct steps are no longer observed; and it seems that penetration of chlorine-containing species and the decolouration reaction occur simultaneously. Because the penetration of chlorine species was in all cases determined by energy dispersive X-ray analysis, the chemical form of the chlorine species (as chloride, hypochloride or chlorate) could not be determined.

(2) The incubation periods decrease with increasing stabilization time. Fibres containing a weak acid co-monomer, which acts as an initiator for nitrile polymerization, have shorter incubation times than fibres which do not contain the catalyst. Both incubation periods can be associated in part with the dense outer skin of the acrylic fibres and with the presence of inert material which initially acts as a barrier, in addition to the usual time required for the establishment of boundary layers.

(3) The rate of the decolouration reaction, measured in most cases from the time to complete decolouration, increases with increasing decolouration temperature. The apparent activation energy for this process for one set of conditions (fibre type, stabilization temperature and stabilization time) was about 6 kcal mol^{-1}. Hence decolouration is a facile reaction.

(4) The hypochlorite reagent destroys and solubilizes that portion of the fibre which has undergone either prefatory or sequent reactions. If the fibre has been stabilized for only a short

time and incubation periods are noted, a porous network of acrylic polymer remains after decolouration. For very short stabilization times, the porous network of acrylic polymer swells during decolouration, the final fibre diameter being greater than the original diameter. Due to internal swelling pressures, the network tends to split axially. For longer stabilization times, the diameter of the final fibre is less than the original diameter. For even longer stabilization times, no porous network remains after decolouration.

(5) The existence of the acrylic network after partial stabilization and decolouration demonstrates that the prefatory reactions are not complete under the conditions tested in this work. Even in fibres undergoing diffusion-controlled kinetics, wherein a well-defined dark outer mantle advances inward at a rate proportional to the square root of time, acrylonitrile units in the mantle and core regions continue to undergo the prefatory reactions. It is expected, but not demonstrated here, that the prefatory reactions are faster in the mantle because of the presence of oxygen.

(6) The rate of decolouration increases with increasing stabilization time under both oxidative and inert stabilization conditions. For CHT fibres at 226° C in air, the rate of decolouration as measured by the time to complete decolouration at 50° C, t_{dec}, depends upon stabilization time, t_{stab}, as: $1/t_{\text{dec}} = 5 \times 10^{-8}$ $(t_{\text{stab,sec}})\,\text{sec}^{-1}$. The decolouration rate increases with increasing stabilization temperature and decreases when stabilization is effected under inert conditions. For extended stabilization times, the decolouration rate should go through a minimum and then increase again as the polymer begins to undergo release of heteroatoms.

(7) Because the decolouration reaction shows no obvious change in rate as the reaction progresses from the dark outer mantle to the light core of fibres which have undergone diffusion-limited stabilization, the reactivities to hypochlorite of the groups formed from the prefatory and sequent reactions are equivalent. This can occur if: (a) the reactivity of the groups formed by the prefatory reactions is not influenced by the groups formed by the sequent reactions; or (b) the prefatory groups are transformed into sequent groups during the chloride atom penetration and decolouration processes and then undergo the decolouration reaction. Confirmatory evidence for the equivalence of reactivity is obtained by short-term stabilization under inert and oxidative conditions.

(8) ^{13}C-NMR spectra of the polymer residue after the decolouration reaction shows that the stereospecificity of the residual acrylic polymer is the same as that of the starting fibre. The rate of polymerization of nitrile groups is therefore not affected by syndiotactic or isotactic placements, as has been suggested previously. One reason may be the facile rearrangement of the stereostructure of the ultimate units of the growing nitrile chains at the temperatures of stabilization.

(9) The penetration of chlorine-containing species, as measured by the incubation time t_1, demonstrates a degree of heterogeneity from filament to filament within a treated yarn bundle. The degree of heterogeneity is very high for fibres which do not contain a weak acid comonomer. The effect could be due to variations in fibre formation, the stabilization process or the decolouration process. It is believed but not confirmed, that most of the variability results from the stabilization process.

(10) Hypochlorite ion is a facile electrophile in the presence of a nucleophile such as pyridine. The relatively oxidative resistant pyridine is rapidly attacked by hypochlorite. Similar reactions may occur in stabilized acrylic fibres wherein the nucleophilic nitrogen is attacked, leading to ring opening followed by attack on any residual unsaturation.

(11) Nitrile polymerization is initiated by three types of groups: those present in the fibre prior to stabilization, those created under oxidative conditions and those created under inert conditions. The overall rate of polymerization is greatest when initiator groups are present in the as-formed fibre, for instance, fibres that contain catalytic additives. Under the conditions of test examined, these active groups are exhausted before all nitrile units have polymerized. The overall rate of polymerization is slower when initiators have to be formed under oxidative stabilization conditions and is slower still when initiators are formed under inert conditions. Some fibres contain catalytic amounts of itaconic acid, which is present in textile fibres to act as a dye site. The quantity present may not be optimal for efficient stabilization.

(12) Hot aqueous sulphuric acid will dissolve the precursor acrylic fibre and will destroy/solubilize

that portion of the fibre which has undergone only the prefatory reactions, leaving behind a residue of sequent-reacted material. The residue obtained from sulphuric acid treatment of fibres undergoing diffusion-controlled stabilization is in the form of an annulus which corresponds to the dark mantle. The density of the annulus increases with increasing stabilization time. The residue from fibres undergoing reaction-limited stabilization is distributed throughout the fibre cross-section, and also exhibits porosity and a density which increases with increasing time of stabilization.

(13) The process of hypochlorite and sulphuric acid attack on partially stabilized fibres lead to the following model of stabilized fibre microstructure: during stabilization, the morphology changes from the homogeneous chemical composition of ordered and disordered acrylic phases to interpenetrating networks of reacted and unreacted material, and finally to a structure dominated by the sequent-reacted material. The interpenetrating networks consist of segments of acrylic molecules unaffected by stabilization, prefatory-reacted or sequent-reacted material. The composition of the interpenetrating networks and the final sequent structure depends upon process conditions.

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