The Photochemical Degradation of Polyamides and Related Model N-*Alkylamides*

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Analogous products to those obtained from exposure of simple model N-*alkylamides to u.v. light, in oxygen or under anaerobic conditions, have been sought in a concurrent investigation of the photodegradation of polyamides (chiefly 6.6 nylon) in u.v. light and sunlight. The polymer degradation has been characterized by measurement of yarn tenacity losses under different conditions, and correlation of these with changes in intrinsic viscosity, u.v. absorption and end-groups. Chemical changes occurring, detected by analysis of the hydrolysed polymer, indicate the formation of aldehyde and primary amide end-groups, and a smaller number of* n-*pentylamino and* n-*pentanoyl end-groups. The results for both* N-*alkylamides and polyamides, can be interpreted by postulating two types of reaction: a photolysis into both free radicals and smaller molecules, occurring at short wavelengths and independent of oxygen, and a photosensitized autoxidation, occurring at longer wavelengths, involving oxidative attack predominantly at the methylene group adjacent to the* N *atom of the molecule, and subsequent decomposition of the derived radical* R.CO.NH.CH(O·).R′. *The more rapid loss of tenacity observed with titanium dioxide delustered yarns containing no oxidation inhibitors is due to increased photodegradation around the delustrant particles; the same products result as with bright yarns.*

EXPOSURE to sunlight under natural conditions causes a deterioration in the desirable properties of many artificial and natural textile materials. The changes which occur, which can be reproduced using artificial light, manifest themselves as a loss of strength and elasticity of the individual fibres. There is an accompanying reduction in the molecular weight of the fibre molecules, and slight changes in its chemical constitution can be detected.

The present work is confined to an investigation of the photochemical degradation of polyamide material used in the manufacture of nylon (in particular 6.6 nylon). Although from the practical point of view, the main interest lies in the degradation occurring in the presence of oxygen, a straight photolysis of the polyamide chains was also studied. To gain some insight into the type of chemical changes to be expected, a parallel investigation of the photochemical decomposition of aliphatic *N*-alkylamides of the type $H(CH_2)_mCO.NH(CH_2)_nH$ (where $m+n=11$ or 12) was also carried out.

The comparatively meagre information available in the literature on the photo-decomposition of amides has recently been augmented by a comprehensive study of the photo-oxidation of *N*-pentyl hexanamide and analogous amides[1]. With light of wavelength greater than 3 000 Å, acids, aldehydes, primary amide, carbon monoxide and dioxide were obtained; oxidative attack occurred primarily at the methylene group adjacent to the nitrogen atom of the amide molecule, resulting in peroxidation at this point with subsequent breakdown to give an aldehyde and primary amide. Compounds of the type RCO.NH.C(R″)$_2$R′ (where R″ is alkyl) were found to be resistant to oxidation. Independent work in these laboratories has followed similar lines; however, as shorter wavelength light was not excluded, products from photolysis were also observed. *N*-acylamides have also been reported as major products of the autoxidation of *N*-alkylamides[2]. These are formed from the alternative modes of breakdown of the peroxy radical RCO.NH.CH(OO·)R′.

Although considerable work has been published on the photodegradation of nylon[3–10], few attempts have been made to study chemical changes occurring in the polymer. Both chainbreaking and crosslinking have been shown to occur, the latter chiefly at shorter wavelengths; in the absence of oxygen, the formation of hydrogen, carbon monoxide and hydrocarbons has been observed with both 6.6[11] and 6 nylon[12]. Evidence for the role played by water is conflicting[3, 13, 14].

In the present investigation, the results from the work with *N*-alkylamides led to a search for similar products as end-groups in the cleaved polymer chains. A study was also made of the conditions under which both bright (containing nil delustrant) and delustred yarns undergo degradation as measured by loss in tenacity, and the latter was related to changes in other physical and chemical properties occurring on exposure of polyamide fibres to sunlight.

EXPERIMENTAL

Apparatus

The lamp used in experiments with artificial light was an air-cooled, 1 kW high pressure mercury vapour lamp, having a virtual point source. The light from three circular apertures in the lamp housing was focused into almost parallel beams, *ca.* 9 cm across, by water-filled quartz flasks. A fourth aperture led to a photocell actuating an integrating meter which measured the total light energy in arbitrary units on a counter. Chance glass filters were used to select various wavelengths of light.

The model amides were exposed in quartz flasks. In the experiments using artificial light, polymer film and yarn samples were exposed in gas-tight metal cells with plane windows of quartz or Pyrex.

Materials

The *N*-alkylamides, all liquid at 25°C, were prepared by reacting equivalent amounts of the aliphatic amine and carboxylic acid chloride in benzene or ether, in the presence of a slight excess of pyridine at a temperature below 30°C. The amide, after washing with dilute hydrochloric acid, ten per cent sodium carbonate solution and water, was purified twice by distillation under reduced pressure. Details are as follows:—*N*-hexylhexanamide, b.pt 108° to 111°C at 0·07 mm (found C, 72·4; H, 12·7; N, 6·9 per cent); *N*-butyloctanamide, b.pt 125° to 129°C at 0·2 mm (found C, 71·9; H, 12·6; N, 6·8 per cent); *N*-heptylhexanamide, b.pt 132° to 136°C at 0·2 mm (found C, 73·6; H, 12·6; N, 6·4 per cent); *N*-methyl-*N*-pentylhexanamide, b.pt 75° to 76°C at 0·06 mm (found C, 72·3; H, 12·9; N, 7·4 per cent); *N*-(1,1-dimethylbutyl)-hexanamide*, b.pt 81°C at 0·08 mm

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*1,1-Dimethylbutylamine was prepared according to Montagne's method[15].

(found C, 72·5; H, 12·7; N, 7·0 per cent. $C_{12}H_{25}ON$ requires C, 72·3; H, 12·6; N, 7·0 per cent: $C_{13}H_{27}ON$ requires C, 73·2; H, 12·8; N, 6·7 per cent).

Hot pressed films of 6.6, 6.10, 10.6 and 6 nylons free from delustrant were used in small scale experiments involving exposure of polymer to artificial light. For larger scale sunlight exposures, hanks of bright (30 denier, 10 filament, nil titanium dioxide) and delustred (45 denier, 15 filament, 1·6 per cent titanium dioxide) multifilament nylon yarns (supplied by British Nylon Spinners Ltd) were used. The yarns for tenacity measurements were obtained by doubling or trebling low-twist yarns, twisting to 4 or 5 turns per inch and steam-setting. All delustred yarns were free of additives present in commercial yarns to reduce photodegradation[16].

Paper chromatographic analysis

Details of the methods used for the analysis of carboxylic acids and amines are as follows[17]. Using a descending method of development, the solvent for monobasic acids was butanol : 1·5 N ammonia (1 : 1 v/v); for dibasic acids, ethanol : water : conc. ammonia (20 : 4 : 1 v/v); and for amines, butanol : acetic acid : water (4 : 1 : 5 v/v). After drying, the sheets of Whatman No. 1 paper were sprayed respectively with bromocresol green (0·1 per cent in isopropanol) to detect monobasic acids (giving blue spots on a yellow background), with B.D.H. Universal indicator for dibasic acids (red spots on green), and with ninhydrin (0·3 per cent in butanol) for amines (purple spots for primary aliphatic amines after heating for 15 min at 80°C). Aldehyde 2,4-dinitrophenylhydrazones were chromatographed using paper impregnated with phenoxyethanol, and light petroleum as the developing solvent[18].

Exposure of N-*alkylamides to u.v. light*

In most experiments pure oxygen or nitrogen was bubbled slowly (*ca.* 0·5 l./h) through about 160 g of the *N*-alkylamide in a 200 ml quartz flask, placed about 30 cm from the lamp; the amide reached a temperature of about 40°C. Off-gases passed consecutively through two traps cooled in Drikold, Anhydrone and Carbosorb tubes, and a bubbler containing 0·01 N hydrochloric acid. In no experiment was there any indication of the absorption of basic gases by this trap. Carbon monoxide was detected using 'CO-test' tubes containing silica gel impregnated with potassium palladosulphite and estimated with iodine pentoxide[19].

The cold traps condensed a small amount of organic material and water and further volatile material was collected in them by heating the exposed amide to 150°C in a current of nitrogen. Analysis of these products by mass and i.r. spectroscopy and paper chromatography indicated a mixture of *n*-paraffins and 1-olefins, carboxylic acids and an aldehyde which was identified by paper chromatography of its 2,4-dinitrophenylhydrazone.

The bulk of exposed material was distilled under reduced pressure to give a low-boiling fore fraction (*ca.* 10 g), a large middle fraction of unchanged amide, and a residue (*ca.* 5 g). The fore fraction and residue were examined before and after acid (5 N hydrochloric) or alkaline (10 per cent ethanolic sodium hydroxide) hydrolysis by a combination of chromatographic, i.r. and mass spectrometric techniques. The fore fraction was further separated by steam distillation to give a small distillate (*ca.* 1 g) consisting mainly of acids; from the non-volatile material, which consisted largely of unchanged *N*-alkylamide, a solid primary amide (*ca.* 1 g) was obtained by distillation and purified by crystallization. In addition, the viscous residue, on treatment with ether, sometimes yielded a small amount of solid which analysed approximately for a dimer of the parent *N*-alkylamide.

In some experiments, concentration of the gaseous products of the degradation for mass spectrometric analysis was effected by re-circulating the same oxygen through the *N*-alkylamide. (Similar analyses were obtained of the off-gases from exposures *in vacuo*.) The circulating technique was also used to compare the rates of oxygen absorption of selected model amides when exposed to light of different wavelength. The amides compared, *N*-hexyl-hexanamide, *N*-methyl-*N*-pentylhexanamide and *N*-(1,1-dimethylbutyl)-hexanamide, were chosen because of the varying number of hydrogen atoms adjacent to the nitrogen atom of the molecule.

The experiments carried out and the products obtained are summarized in *Table 1*; other details are as follows.

Exp. 1. Unknown amines from the residue hydrolysate had R_f values 0·90, 0·55, 0·39 and 0·30.

Exp. 2. The 'dimer', 0·03 g, m.pt 186° to 189°C (crystallized from ethanol: found C, 72·9; H, 11·8; N, 6·9 per cent, corresponding to an empirical formula $C_{12}H_{23\cdot1}N_{0\cdot97}O_{1\cdot04}$; mol. wt 444·5 corresponding to a C_{24} molecule) is probably two *N*-butyl-octanamide molecules crosslinked in some way. The i.r. spectrum was similar to that of the parent amide but contained additional bands at 8·25, 8·76 and 10·46μ, possibly due to a diamide. Unknown amines from the residue hydrolysate had R_f values 0·84, 0·80, 0·37 and 0·24.

Exp. 4. Mass spectrometric analysis of volatile material, b.pt 87° to 120°C at 0·15 mm, indicated masses 157, 129, 116 and 115 as parent ions. Of these, mass 157 (with a large breakdown ion, mass 142) could be due to *N*-acetylheptylamine; mass 115 was due to hexanamide while mass 129 suggests a methyl homologue of it. However, no methylamine was detected in the hydrolysate. The unknown compound of mass 116 was not *n*-hexanoic acid.

Exp. 5. Mass spectrometric analysis of material, b.pt 130° to 180°C at 11 mm, again showed masses 157, 129 and 116.

Exp. 8. During distillation of the exposed amide *ca.* 0·01 g of *n*-heptylamine was condensed in a cold trap.

Exp. 9. *N*-Butylhexanamide (100 g) was exposed in pure cyclohexane (150 ml); extraction of the solution with dilute hydrochloric acid yielded no amines. The recovered cyclohexane showed no unsaturation.

Exps. 10–12. Rates of oxygen absorption were determined for the three selected *N*-alkylamides (70 g samples in 100 ml quartz flask) in the full beam of the lamp, and with light of wavelength greater than 3 000 Å (Pyrex filter) and 3 500 Å (Chance filter OY 10) only. The comparative rates for wavelengths greater than 2 500 Å were in the order *N*-methyl-*N*-pentylhexanamide: *N*-hexylhexanamide: *N*-(1,1-dimethylbutyl) hexanamide, 2·9 : 1·5 : 1 : The same order was found in the comparison of the last two amides when light of wavelengths greater than 3 000 Å and 3 500 Å was used, the ratios being 4·7 : 1 and 25 : 1 respectively. Products of the degradation included with *N*-methyl-*N*-pentylhexanamide, a non-steam volatile fraction, b.pt

94° to 142°C at 15 mm (0·55 g), which on mass spectrometric analysis showed two molecular ions at masses 129 and 142, probably due respectively to *N*-methylhexanamide and *N*-acetyl-*N*-methylpentylamine. The hydrolysate contained small amounts of methylamine and probably acetic acid.

Chemical investigation of photo-degraded nylons

Nylon films degraded in u.v. light—Films of 6.6, 6.10, 10.6 and 6 nylons were exposed in quartz-windowed cells, in atmospheres of air, nitrogen or *in vacuo,* to the full beam of the lamp for about four days. After hydrolysis of the degraded films by heating at 120°C in a sealed tube with 5N hydrochloric acid for 16 hours, products were separated into volatile and non-volatile acids and bases by a procedure of steam distillation and continuous ether extraction of the hydrolysate under acid and subsequently under alkaline conditions, and examined by paper chromatography. Controls were carried out simultaneously using unexposed films.

(*a*) 6.6 Nylon. After exposure in air at 40° to 50°C for 75 h, films were brittle, brownish in colour and no longer completely soluble in 90 per cent phenol–water; thus 1·66 g of exposed film gave 0·30 g of insoluble material and similar amounts were obtained from experiments in nitrogen and oxygen. Paper chromatographic analysis of the hydrolysate showed:

volatile acids: mostly acetic, some *n*-pentanoic and traces of butyric and propionic acids;
non-volatile acids: adipic acid only;
volatile bases: *n*-pentylamine with traces of possibly the C_1 to C_4 mono-amines;
non-volatile bases: mainly hexamethylenediamine, also traces of other substances with lower R_f values, and an unresolved streak extending to the solvent front.

The hydrolysate from unexposed film gave acetic acid, adipic acid, hexamethylenediamine and traces of *n*-pentylamine.

The analysis of the hydrolysate from films exposed *in vacuo* differed from those exposed in air only in that the amount of *n*-pentylamine was reduced and similar to that in the control.

(*b*) 6 Nylon. Analysis of the hydrolysate from films exposed in air showed the presence of (in addition to 6-aminohexanoic acid) *n*-pentanoic and acetic acid, possibly oxalic and a trace of succinic acid, and *n*-pentylamine and a small amount of a C_4 amine. The control showed acetic acid and the dibasic acids.

(*c*) 6.10 Nylon. The hydrolysate from exposed films contained besides sebacic acid and hexamethylenediamine, acetic and *n*-nonanoic acid, adipic acid and a complex mixture of unidentified dibasic acids incompletely separated on the chromatogram, *n*-pentylamine and a number of ether-insoluble non-volatile bases giving a similar pattern on the chromatogram to that observed with 6.6 nylon. The control showed acetic and adipic acids.

(*d*) 10.6 Nylon. Besides decamethylenediamine and adipic acid, acetic and *n*-pentanoic acids, with traces of butyric and propionic acids, *n*-nonylamine and traces of sundry unresolved non-volatile amines were detected in the hydrolysate.

6.6 Nylon yarn degraded in sunlight—Hanks of 30-denier bright nylon yarn were exposed to sunlight under glass for one year, while control samples were subjected to the same conditions of heat and humidity in

Table 1. Experiments involving the exposure of *N*-alkylamides to u.v. light

Exp. No.	*Model amide*	*Expl conditions*	*Time of exposure h*	*Oxygen uptake ml*	*Products*									
					Off-gases			*Hydrocarbons*[a]		n-*Aldehydes*	n-*Acids*[a, b]		n-*Amides*	*Other products*
					H_2O g	CO_2 g	CO g	n-*Paraffins*	*1-Olefins*		*Free*	*On hydrolysis*		
1	*N*-Hexyl-hexanamide	O_2 flow	76		0·05	0·11		Pentane	Pentene	Hexanal	**Hexanoic** Pentanoic Butyric Propionic Acetic	**Hexanoic** Acetic	Hexanamide	
2	*N*-Butyl-octanamide	O_2 flow	76		0·02	0·11	0·1	**Heptane** Hexane **Pentane**	Heptene Hexene **Pentene**	Butanal	**Octanoic** Butyric Propionic Acetic	**Octanoic** Acetic	Octanamide	'Dimer'
3	*N*-Heptyl-hexanamide	O_2 flow	76		0·03	0·08		**Hexane** Pentane Butane	Hexene **Pentene**	Heptanal	Heptanoic	**Hexanoic** Acetic	Hexanamide	
4	*N*-Heptyl-hexanamide	O_2 Circulating flow	96 97	400				**Hexane** Pentane Butane	Pentene	Heptanal	**Heptanoic** **Hexanoic** Pentanoic Butyric Propionic Acetic	**Hexanoic** Acetic	Hexanamide	*N*-acetyl-heptylamine[c] Unknown compds masses 129, 116
5	*N*-Heptyl-hexanamide	1·6% TiO_2 O_2 Circulating flow	72 72	313		0·18		**Hexane** Pentane Butane	Hexene **Pentene** Butene	Heptanal	**Heptanoic** **Hexanoic** Pentanoic Butyric Propionic Acetic		Hexanamide	*N*-acetyl-heptylamine[c] Unknown compds masses 129, 116

6	*N*-Butyl-octanamide	N_2 flow	91		0·02	0·003	0·03	Heptane	Hexene		Octanoic			
7	*N*-Butyl-octanamide	*In vacuo*	190		*d*		*d*	Heptane	Heptene **Hexene** Pentene Butene		Octanoic			'Dimer'
8	*N*-Heptyl-hexanamide	*In vacuo*	360					Pentane	Pentene		Hexanoic	Hexanoic Acetic		Heptylamine
9	*N*-Butyl-octanamide	N_2 cyclohexane	77											*f*
10	*N*-Hexyl-hexanamide	O_2 Circulating (i) $\lambda > 2500$ Å (ii) $\lambda > 3000$ Å (iii) $\lambda > 3500$ Å	*e* 2750 2250 2400	353 50 12·9	0·14	0·04								
11	*N*-Methyl-*N*-pentyl-hexanamide	O_2 Circulating $\lambda > 2500$ Å	*e* 2275	604	0·14	0·03				Pentanal	**Hexanoic** Acetic	**Hexanoic** Acetic	*N*-methyl-hexanamide[c]	*N*-acetyl-*N*-methyl-pentylamine[c]
12	*N*-(1,1-di-methylbutyl) hexanamide	O_2 Circulating (i) $\lambda > 2500$ Å (ii) $\lambda > 3000$ Å (iii) $\lambda > 3500$ Å	*e* 2750 1850 2250	200 10·4 0·4	0·12	0·04								

a Black type signifies the chief constituent of a group of products.
b The paper chromatographic analysis could not distinguish between formic and acetic acids; the presence of one could mask the other.
c Evidence for these compounds is only indirect.
d Detected but not measured.
e Length of exposure measured in arbitrary light integrating meter units.
f No unsaturation detected in the cyclohexane after exposure.

the dark. Before analysis it was washed thoroughly with soap and water, rinsed and dried. In addition to measurement of intrinsic viscosity and carboxyl and amine end-groups, a large scale hydrolysis of the exposed yarn (50 g) was carried out by heating under reflux in phosphoric acid (200 ml, 65 per cent w/w) in a current of nitrogen for 15 h, estimating the carbon dioxide and carbon monoxide formed. Volatile acids produced were separated by distillation in steam through a fractionating column, and estimated by titration with 0·02 N sodium hydroxide. After removal of non-volatile acids by continuous ether extraction, sodium hydroxide (350 ml, 40 per cent w/w) and methanol (350 ml) were added and volatile bases separated by distillation. Ammonia distilled with the methanol and volatile amines with the subsequent water; they were estimated separately by titration with 0·02 N hydrochloric acid. This sequence of operations was repeated with the control yarn, and also without any yarn to obtain blank measurements. The volatile acids and bases, and the impurities in the mother liquors from a crystallization of the ether-extracted non-volatile acids, were recovered for paper chromatographic analysis. The results of the analysis are given in *Table 2*.

Table 2. Analysis of bright 6.6 nylon yarn degraded by exposure to sunlight

			Degraded yarn	*Control yarn*
Carboxyl end-groups g equiv./10^6 g polymer			117	82
Amine end-groups g equiv./10^6 g polymer			20	39
Intrinsic viscosity in 90% phenol–water			0·54	0·82
On hydrolysis	Carbon dioxide g equiv./10^6 g polymer		10·2	2·3
	Carbon monoxide g equiv./10^6 g polymer		7·6	1·0
	Volatile acids g equiv./10^6 g polymer		69·2[a]	33·0[b]
	Volatile bases	methanol distillate g equiv./10^6 g polymer	85·0[c]	14·3[c]
		aqueous distillate g equiv./10^6 g polymer	103·7[d]	9·2[e]

[a] Mostly *n*-pentanoic and acetic with some butyric and traces of hexanoic and propionic acids. The non-volatile acids included glutaric and succinic in addition to adipic.

[b] Acetic acid.

[c] Nessler reagent indicated ammonia.

[d] Ammonia containing 10 to 20 per cent *n*-pentylamine.

[e] Ammonia containing 2 to 5 per cent *n*-pentylamine.

Development of chemical tests on photo-degraded bright 6.6 nylon yarn—Aldehyde, peroxide and pyrrole groups were detected in bright 6.6 nylon yarn degraded by exposure to sunlight and u.v. light in air, by the application of slightly modified well-known colorimetric tests. Formation of the last grouping was due to thermal action and independent of the presence of oxygen.

The tests applied were as follows:

(*a*) For aldehyde (—CHO) groups with *o*-dianisidine[20]: on boiling 0·2 g samples of yarn for 2 min with 10 ml of a 5 per cent solution of *o*-dianisidine in acetic acid, photo-degraded samples gave a deep orange-brown solution while the blank reagent colour was pale greenish-brown.

(*b*) For carbonyl (C═O) groups with 2,4-dinitrophenylhydrazine: with a 0·7 per cent solution of the reagent in 8 N hydrochloric acid, 0·5 g yarn samples dissolved in 20 ml of the reagent solution in the cold producing different depths of orange colour depending on the degree of degradation.

(*c*) For pyrroles with Ehrlich's reagent: 0·2 g samples of yarn were dissolved in 2 ml of reagent (2 per cent *p*-dimethylaminobenzaldehyde in concentrated hydrochloric acid) and diluted with 5 ml of ethanol when a reddish-purple colour developed.

(*d*) For peroxides[21]: ammonium thiocyanate (1 g) in de-aerated methanol (50 ml), containing 1 ml 25 per cent sulphuric acid, and de-aerated formic acid (150 ml, 90 per cent w/w) was shaken with finely powdered ferrous ammonium sulphate (0·2 g) under nitrogen. Yarn samples (0·2 g) were immersed in the freshly prepared reagent (5 ml) under nitrogen, and developed a red coloration after a few minutes which persisted after dissolution of the yarn by warming.

Conditions affecting loss of tenacity and extensibility of 6.6 nylon yarn on exposure to u.v. light—Bright and delustred yarns were exposed to u.v. light under different conditions of atmosphere and humidity at different wavelengths and the resultant losses in tenacity and extensibility used to measure the amount of degradation. After exposure, yarns were conditioned overnight at 20°C and 65 per cent relative humidity prior to testing, either on a Goodbrand single thread pendulum-type machine or on a Cambridge extensometer.

The properties of the experimental yarns, from which no attempt was made to remove spinning-finish, were as follows:

60-denier bright, 20 filament, nil TiO_2: tenacity 324 g, extensibility 15·0 per cent
90-denier bright, 30 filament, nil TiO_2: tenacity 465 g, extensibility 17·8 per cent
90-denier delustred, 30 filament, 1·6 per cent TiO_2: tenacity 492 g, extensibility 19·2 per cent.

The four wavelength regions investigated were obtained by using quartz (transmitting all wavelengths) or Pyrex (above 3 000 Å) windows in the exposure cells, or by interpolating filters (OY 10, above 3 500 Å; OY 4, above 5 000 Å) in the light beam. In comparing the effect on yarn of light of different wavelengths, the periods of exposure given were inversely proportional to the amount of light transmitted by the filters, this being obtained both from actinometric measurements and by calculation from the filter transmission curves.

The results were as follows. The presence of moisture had little effect on the degradation. With bright yarn there was a small increase in the loss of strength suffered by samples exposed under dry rather than wet conditions. With delustred yarn there was little difference using all wavelengths of light, but above 3 000 Å a slight enhancement of degradation was observed if moisture was present. Although some loss of tenacity was observed in exposures *in vacuo* below 3 000 Å, bright and delustred yarns being degraded equally, the major part of the degradation was undoubtedly due to the presence of oxygen. The shorter wavelength light was most effective in producing loss in strength with both bright and delustred yarns which were affected equally below 3 000 Å. At higher wavelengths, delustred yarn was degraded much more rapidly than bright, being about twice as susceptible to light above 3 000 Å and about four times to light above 3 500 Å. Degradation was still appreciable with light above 5 000 Å at which wavelength bright yarn was comparatively unaffected.

The relation between loss of strength and other changes in physical and chemical properties of 6.6 nylon yarn on exposure to sunlight—A correlation between the loss of strength and changes in intrinsic viscosity, end-groups and u.v. absorption (cf. *Figure 1*) occurring on exposure of 6.6 nylon yarn to sunlight was obtained by exposing bright and delustred yarns under glass for varying periods of time and then subjecting them to analysis. For the measurements of loss of tenacity the yarns used were the 60- and 90-denier bright, and 90-denier 1·6 per cent delustred, high-twist yarns described above; for other measurements requiring larger samples, hanks of ordinary bright and delustred yarn were exposed. End-group measurements (expressed as g equiv./10^6 g polymer) comprised carboxyl*, amine†, acyl and amide; the last two were determined as the amount of volatile acids or ammonia liberated on hydrolysis, and estimated as described above.

The variation of end-groups, intrinsic viscosity, etc., with exposure time (measured in hours of daylight) and loss of tenacity is shown in *Figures 2* to *10*. In comparing graphs for bright and delustred yarns it should be

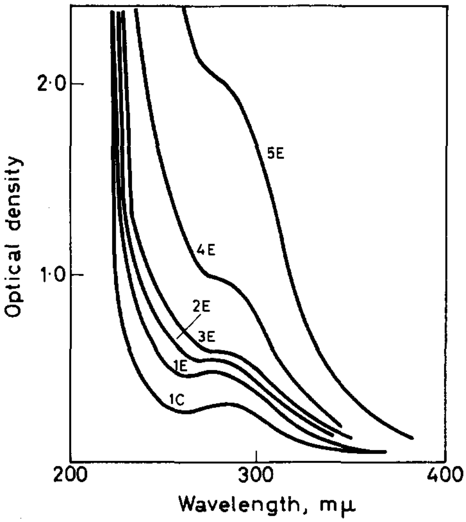

Figure 1—Ultra-violet absorption of sunlight-degraded, delustered 6.6 nylon yarns; increase with exposure time up to five months. (Delustrant removed; 1% solution in 8 N hydrochloric acid, 1 cm cell). C, control; E, exposed

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*By titration in hot benzyl alcohol with 0·1 N potassium hydroxide in ethylene glycol, using phenolphthalein as indicator.

†By titration in 2:1 w/w phenol-methanol with aqueous 0·05 N hydrochloric acid, using thymol blue as indicator.

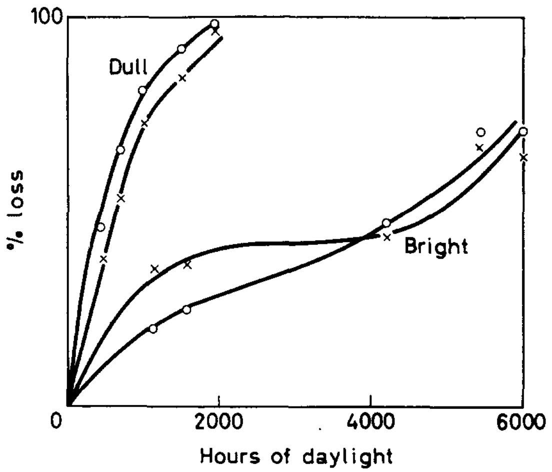


Figure 2—Variation of loss of tenacity and extensibility with exposure time for sunlight-degraded 6.6 nylon yarns (○ tenacity; × extensibility)

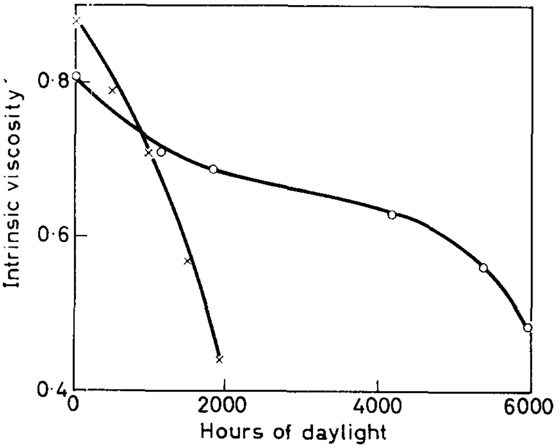
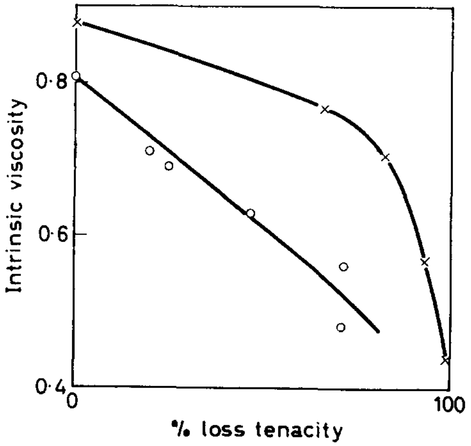


Figure 3—Variation of intrinsic viscosity in 90% phenol–water with exposure time for sunlight-degraded 6.6 nylon yarns (○ bright; × delustred)

Figure 4—Volume of intrinsic viscosity with loss of tenacity (○ bright; × delustred)



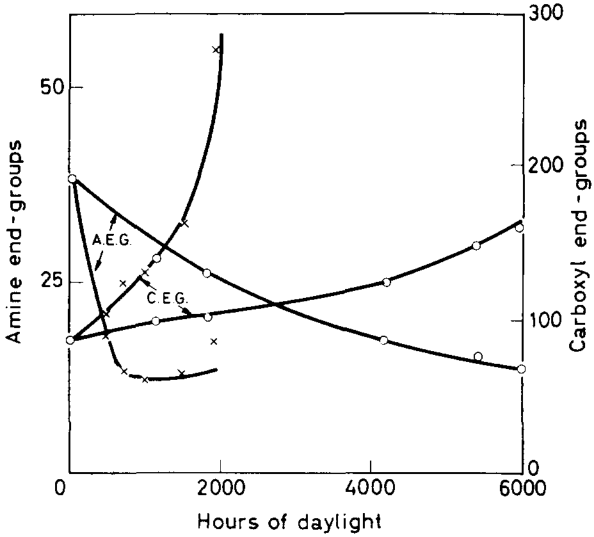


Figure 5—Variation of amine and carboxyl end-groups with exposure time for sunlight-degraded 6.6 nylon yarns (O bright; × delustred)

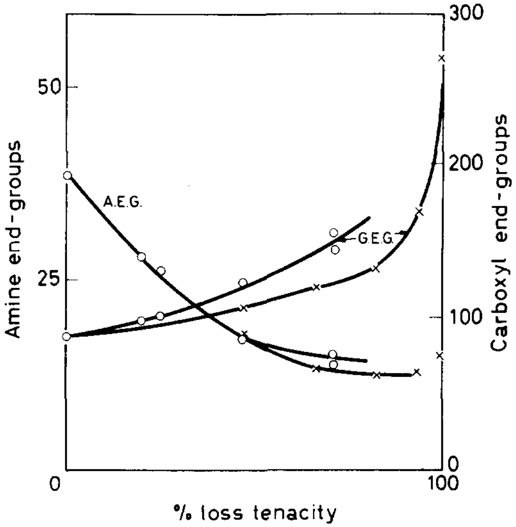


Figure 6—Variation of amine and carboxyl end-groups with loss of tenacity (O bright; × delustred)

noted that the first 1 000 h exposure for delustred, and from 2 000 to 3 500 h for bright, was winter daylight and the rest summer; this will account for the S-shape of some of the curves for bright yarn. Also the denier of the delustred yarn was greater than that of the bright; comparison between 60- and 90-denier bright yarns indicated that the latter degraded rather more quickly. Since the tenacity measurements were carried out on specially displayed samples while other measurements were performed on less uniformly exposed yarns, the average loss of tenacity in the hank would therefore be less than in the prepared samples, the values from which were used in plotting the curves.

The chief points to be noted from the graphs are as follows. The rate of loss of tenacity and extensibility decreased with increased exposure time,

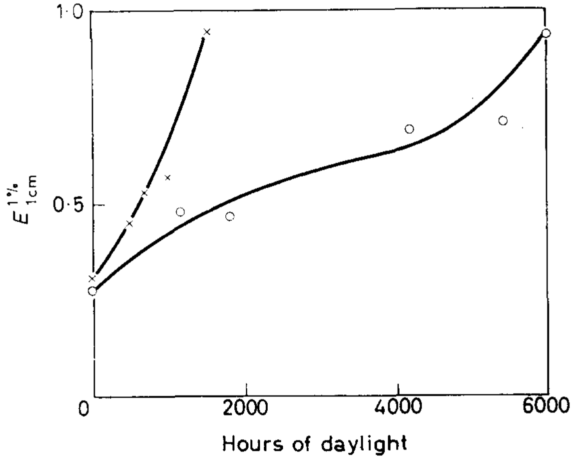


Figure 7—Variation of u.v. absorption at 280 mμ with exposure time for sunlight-degraded 6.6 nylon yarns (○ bright; × delustred; in 8N hydrochloric acid)

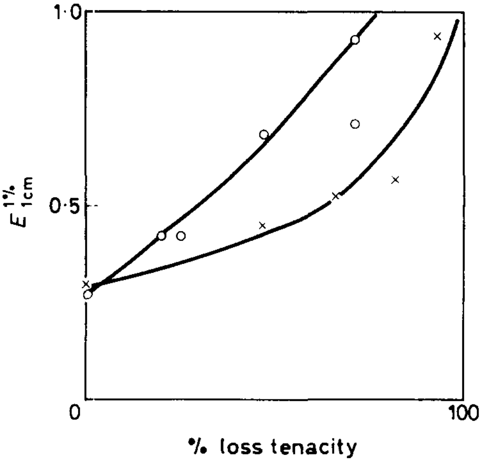


Figure 8—Variation of u.v. absorption with loss of tenacity (○ bright; × delustred)

the delustred yarn losing strength much more rapidly than the bright. This loss of strength was accompanied in both yarns by a progressive decrease in intrinsic viscosity and hence molecular weight. There was a drop in amine end-groups, which approached a constant value very quickly in the delustred yarn, and progressive increase in carboxyl end-groups, u.v. absorption, acyl and amide end-groups. In all cases the change in these properties with exposure time was more rapid with the delustred than with bright yarn. As regards loss of strength, however, the delustred yarn

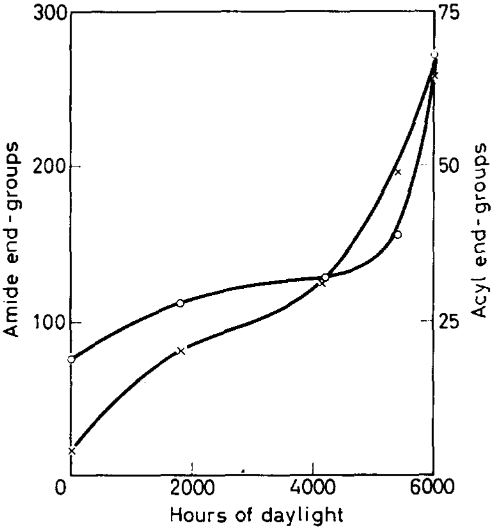


Figure 9—Variation of amide and acyl end-groups with exposure time for sunlight-degraded 6.6 bright nylon yarn (O acyl; × amide end-groups)

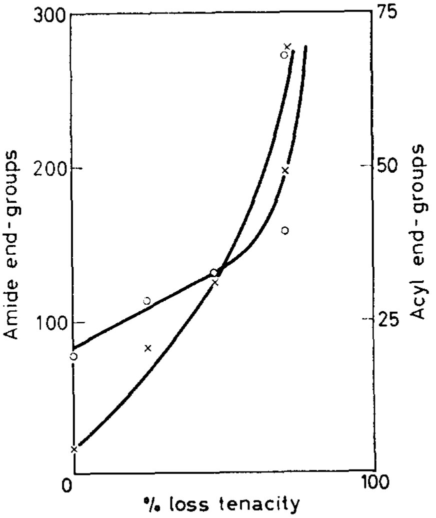


Figure 10—Variation of amide and acyl end-groups with loss of tenacity (O acyl; × amide)

suffered rather less degradation (as characterized by changes of end-groups etc.) for the same loss of tenacity than the bright, or, conversely, for the same amount of degradation the delustred yarn lost more strength than the bright. In general the rate of degradation (i.e. chemical change as opposed to loss of tenacity) increased with exposure time.

DISCUSSION

The photodegradation of N-*alkylamides*

The products from the u.v. degradation of *N*-alkylamides differed somewhat depending on whether or not oxygen was present. It is thus possible to distinguish two types of decomposition, a photochemical oxidation, and a direct photolysis of the molecules occurring with light of somewhat shorter wavelength independently of the atmosphere.

The photolysis—The products of photolysis were carbon monoxide, water, hydrocarbons, carboxylic acids and *N*-alkylamides having different chain lengths from the parent compound; in addition there was some slight evidence for the formation of primary amine.

Although accurate bond dissociation energies are not known for all the bonds in the amide molecule, the known values indicate that the C—N bonds are probably the weakest[22] and of the two, the NH—CH$_2$ bond is probably somewhat weaker than the NH—CO bond the energy of which will be enhanced by the resonance energy of the amide group. However, such values are for a homolytic splitting into two free radicals whereas intramolecular fission into two complete molecules might occur more readily.

The following reaction mechanisms, involving both types of reaction can be postulated to account for the products of photolysis.

$$\mathrm{R.CH_2.CH_2.CH_2.CO.NH.CH_2.CH_2.R' \rightarrow R.CH_2.CH_2.CH_2.CO. + .NH.CH_2.CH_2.R'} \tag{1}$$

$$\mathrm{R.CH_2.CH_2.CH_2.CO. \rightarrow R.CH_2.CH_2.CH_2. + CO} \tag{2}$$

$$\mathrm{2R.CH_2.CH_2.CH_2. \rightarrow R.CH_2.CH_2.CH_3 + R.CH_2.CH{=}CH_2} \tag{3}$$

$$\mathrm{R.CH_2.CH_2.CH_2. + XH \rightarrow R.CH_2.CH_2.CH_3 + X.} \tag{4}$$

$$\mathrm{R'.CH_2.CH_2.NH. + XH \rightarrow R'.CH_2.CH_2.NH_2 + X.} \tag{5}$$

$$\mathrm{R'.CH_2.CH_2.NH. \rightarrow polymer\,(?)} \tag{6}$$

$$\mathrm{R.CH_2.CH_2.CH_2.CO.NH.CH_2.CH_2.R' \rightarrow R.CH_2.CH_2.CH_2.NH.CH_2.CH_2.R' + CO} \tag{7}$$

$$\mathrm{R.CH_2.CH_2.CH_2.NH.CH_2.CH_2.R' \rightarrow R.CH_2.CH_2.\dot{C}H_2.NH. + .CH_2.CH_2.R'} \tag{8}$$

$$\mathrm{R.CH_2.CH_2.CH_2.CO.NH.CH_2.CH_2.R' \rightarrow R.CH{=}CH_2 + .CH_3.CO.NH.CH_2.CH_2.R'} \tag{9}$$

$$\mathrm{R.CH_2.CH_2.CH_2.CO.NH.CH_2.CH_2.R' \rightarrow R.CH_2.CH_2.CH_2.CO.NH_2 + CH_2{=}CH.R'} \tag{10}$$

Analogous reactions to these have been put forward by previous workers to explain photolysis in primary amides[23] and alkyl esters[24]. Which reactions occur in the photolysis of *N*-alkylamides can be deduced from the products reported in *Table 1*.

Carbon monoxide can arise through the reactions of equations (2) or (7). The former, which involves a free radical mechanism, is supported by the fact that the corresponding alkane from the radical R.CH$_2$.CH$_2$.CH$_2$. was one of the chief hydrocarbon products. Thus *N*-butyloctanamide gave *n*-heptane, and *N*-heptylhexanamide yielded *n*-pentane. However, the evidence for the formation of amine, which should also result from this reaction, was not definite, its formation only being detected in experiment 8 and the possibility cannot be excluded that it was derived in some way by hydrolysis of the parent amide.

Hydrogen-transfer reactions of the type given by equations (4) and (5) (where XH represents a hydrogen donor, probably an *N*-alkylamide molecule) could quite easily occur in reactions in a liquid medium of essentially hydrocarbon character and should produce corresponding unsaturation. However, in experiment 9, performed in cyclohexane for the direct purpose of detecting unsaturation in the solvent, none was observed. Such conditions were also favourable for the production of amines but none was observed.

There was no evidence for the formation of carbon monoxide by the reaction of equation (7) as secondary amines of the required type were not found. Thus although the evidence is not complete, the reaction of equation (1) seems a probable one and provides a satisfactory explanation of the formation of the paraffin $R.CH_2.CH_2.CH_3$. The fate of the amino radical is undecided but seems to favour equation (6) rather than (5).

The occurrence of crosslinking reactions is evidenced by the formation of the dimer of *N*-butyloctanamide isolated in experiment 7, probably by the combination of hydrocarbon-type radicals, the amide groups being preserved intact.

There is indirect evidence for the formation of *N*-acetylamines by the reaction of equation (9) [although the experiments concerned were actually carried out in oxygen, the photolytic process of equation (9) is unlikely to be affected by this] based on the fact that in general hydrolysis of the material of somewhat lower boiling-point than the parent amide always yielded small amounts of acetic acid. In addition mass spectrometric analysis of low-boiling fractions from the experiments 4 and 5 with *N*-heptylhexanamide showed the presence of a compound of mass 157, together with a large breakdown mass of 142, corresponding to *N*-acetylheptylamine and the ion resulting from the loss of a methyl group.

The corresponding olefins from equation (9) were not found in every experiment, though 1-hexene was indeed the only olefin detected in experiment 6 with *N*-butyloctanamide under nitrogen, and the predominant one in experiment 7 with the same amide *in vacuo*. The model amides derived from hexanoic acid should yield 1-butene which was detected in some experiments. Additional olefins observed to the ones required by equation (9), were formed possibly by similar fissions occurring at other points in the molecule. In particular the formation of 1-pentene in experiments with the hexanoic amides, and 1-heptene from the octanoic ones, seems to indicate a reaction of the type of equation (11).

$$R.CH_2.CH_2.CH_2.CO.NH.R'' \rightarrow R.CH_2.CH{=}CH_2 + H.CO.NH.R'' \qquad (11)$$

Formyl derivatives were never identified; hydrolysis should yield formic acid which was not distinguishable from acetic acid by the method of paper chromatographic analysis employed.

The photo-oxidation—The photo-oxidation was studied under conditions in which photolysis could still occur. The main additional products were carbon dioxide, aldehyde and primary amide with enhanced formation of water, carboxylic acids and possibly paraffinic hydrocarbons.

Previous workers have made similar observations[1,2], and attributed the formation of these products to an oxidative attack occurring predominantly at the methylene group in the α-position to the nitrogen atom of the amide group. Assuming peroxidation to occur at that point by the reactions of equations (12) to (14), then breakdown of the derived alkoxy radical [equation (15)] can occur in several ways [equations (16) to (19)].

$$\mathrm{R.CO.NH.CH_2.R' + X. \longrightarrow R.CO.NH.\dot{C}H.R' + XH} \tag{12}$$

$$\mathrm{R.CO.NH.\dot{C}H.R' + O_2 \longrightarrow R.CO.NH.C(OO.)H.R'} \tag{13}$$

$$\mathrm{R.CO.NH.C(OO.)H.R' + XH \longrightarrow R.CO.NH.C(OOH)H.R' + X.} \tag{14}$$

$$\mathrm{R.CO.NH.C(OOH)H.R' \longrightarrow R.CO.NH.C(O.)H.R' + .OH} \tag{15}$$

$$\mathrm{R.CO.NH.C(O.)H.R'} \left\{ \begin{array}{lr} \xrightarrow{\mathrm{X.}} \mathrm{R.CO.NH.CO.R' + XH} & (16) \\ \xrightarrow{\mathrm{XH}} \mathrm{R.CO.NH.C(OH)H.R' + X.} & (17) \\ \longrightarrow \mathrm{R.CO.NH. + OCH.R'} & (18) \\ \longrightarrow \mathrm{R.CO.NH.CHO + .R'} & (19) \end{array} \right.$$

The reactions of equations (17) and (18) can ultimately result in the same products. Thus, *N*-(1-hydroxyalkyl)-amides of the type depicted in equation (17) appear to be inherently unstable, the only compounds reported in the literature being formed by condensation of primary amides with formaldehyde[25] or chloral and its homologues[26] (attempts to extend this reaction to the higher aldehydes resulted in the formation of *N*,*N*'-alkylidenediamines[27, 28]) and even the hydroxymethyl derivatives are decomposed slowly in water[29]. Thus the subsequent spontaneous decomposition will give the required aldehyde and primary amide. Assuming the amide radical can pick up a hydrogen atom, then these products are also derived from equation (18).

In contrast to other reports[2], the diacyl amides formed from the reactions of equations (16) and (19) were not detected. Thus acids of the type R'.COOH were not found in the hydrolysates of the degraded *N*-alkylamide fractions; similarly *N*-formylhexanamide, if present at all, contributed only a comparatively insignificant peak to the complex mass spectrum of the low-boiling fractions from experiments 4 and 5. However, there is evidence for the occurrence of the reaction of equation (19) from the hydrocarbons detected. Thus *N*-hexylhexanamide should give *n*-pentane and *N*-heptylhexanamide *n*-hexane, and both were identified in experiments with these compounds.

If the molecule XH in the above schemes represents a molecule of *N*-alkylamide, then a chain reaction is established by the reactions of equations (13) and (14), the initiation step being that in equation (1), the resultant acyl radical playing the role of the species X. in equation (12). The aldehyde (corresponding to XH) was never found although the corresponding acid was invariably detected. A possible source of this acid is from the reaction of the acyl radical with oxygen and decomposition of the resultant per-acid. The acid derived by oxidation of the aldehyde formed from the amine segment of the molecule was in general observed and will arise by a similar mechanism. Some of the carbon dioxide formed in these photo-oxidations may originate from an alternative decomposition of such per-acids to the alkene and water[30] [equation (20)]. In general water will arise from any hydrogen abstraction reaction involving hydroxyl radicals.

$$R.CH_2.CH_2.CO.OOH \rightarrow R.CH{=}CH_2 + H_2O + CO_2 \qquad (20)$$

The reported increased stability towards photo-oxidation, as measured by the rate of oxygen uptake, conferred by substituting the H atoms of the methylene group adjacent to the N atom, in the amine segment of the molecule, with alkyl groups[1] was also found in the present work, confirming that the oxidative attack occurs predominantly at this point. The effect was less noticeable in the presence of short wavelength light when photolytic reactions also occur.

The photodegradation of polyamides

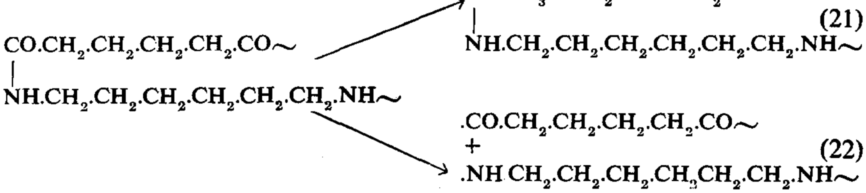
The loss of strength of nylon yarns on exposure to light is undoubtedly due to chemical degradation; thus even with slight losses of tenacity it was possible to detect chemical changes in the fibres.

For photodegration to occur the presence of oxygen is necessary at longer wavelengths whereas at shorter wavelengths it is not, conforming to the concepts of respectively a photosensitized oxidation and a photolysis[3,4]. (The presence of water vapour was found to have little or no effect.)

Hydrolysis of photo-degraded nylon yielded, with 6.6 polymer, in addition to hexamethylenediamine and adipic acid, carbon monoxide, carbon dioxide, *n*-pentanoic acid, lesser amounts of other mono-carboxylic acids, ammonia, *n*-pentylamine, lesser amounts of lower monobasic amines, and traces of higher amines of unknown constitution. In addition, as found by other workers[31], aldehyde groups could be detected in the unhydrolysed yarn. These products can be explained by proposing reactions to occur in the polyamide chain analogous to those found with the model *N*-alkylamides.

The photolysis—In the process of photolysis occurring at wavelengths below 3 000 Å, both direct scission of the polyamide chains and crosslinking should result. Evidence for the latter lies in the formation of the phenol-insoluble material produced on exposure of nylon films to the unfiltered beam from the u.v. lamp. Unfortunately the nature of the crosslinking was not disclosed by the examination of the insoluble polymer, though chemically it behaved on hydrolysis like the parent material.

The probable scissions of, for example, the 6.6 nylon chains are as follows.



$$\begin{array}{l} CO.CH_2.CH_2.CH_2.CH_2.CO\sim \\ | \\ NH.CH_2.CH_2.CH_2.CH_2.CH_2.CH_2.NH\sim \end{array} \rightarrow \begin{array}{l} CO.CH_3 + CH_2{=}CH.CH_2.CO\sim \\ | \\ NH.CH_2.CH_2.CH_2.CH_2.CH_2.CH_2.NH\sim \end{array} \qquad (21)$$

$$\rightarrow \begin{array}{l} .CO.CH_2.CH_2.CH_2.CH_2.CO\sim \\ + \\ .NH\,CH_2.CH_2.CH_2.CH_2CH_2.CH_2.NH\sim \end{array} \qquad (22)$$

$$.CO.CH_2.CH_2.CH_2.CH_2.CO\sim \rightarrow CO + .CH_2.CH_2.CH_2.CH_2.CO\sim \qquad (23)$$

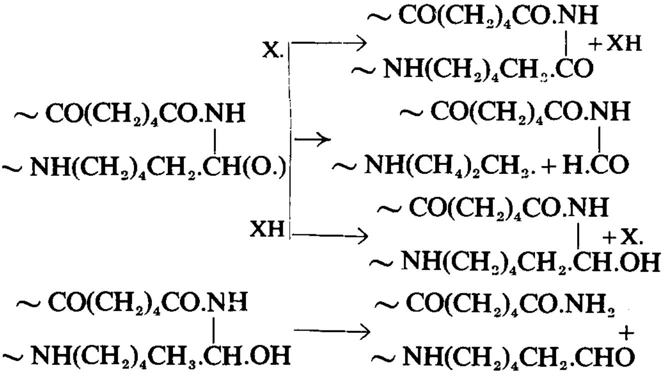
$$.CH_2.CH_2.CH_2.CH_2.CO\sim + XH \rightarrow CH_3.CH_2.CH_2.CH_2.CO\sim + X. \qquad (24)$$

The sequence of reactions of equations (22) to (24) thus explains the production of *n*-pentanoic acid on hydrolysis of photo-degraded 6.6 nylon. With 6.10 and 6 nylons the corresponding products would be *n*-nonanoic acid and *n*-pentylamine, which were in fact identified. The reaction of equation (21) should produce acetic acid on hydrolysis; however, acetyl groups were already present in the undegraded polymer due to the addition of acetic acid added as stabilizer during its manufacture. There was some evidence for the accompanying unsaturated fragment insofar as traces of a C_4 acid were detected in the experiments with 6.6 nylon, and of a possible C_4 amine with 6 nylon. The fate of the amine radical end-groups in equation (22) is not known.

Due to the rigid nature of the polymer, disproportionation reactions between radicals, of the type in equation (3), are improbable. The hydrogen donor XH in equation (24) is thus most likely a methylene group in an adjacent polyamide chain.

Although photolytic reactions of this type occur only with light of short wavelength, it is interesting that *n*-pentanoic acid was detected in the hydrolysate of 6.6 nylon yarn exposed to sunlight behind glass, indicating that these reactions can occur under such conditions.

The photo-oxidation—By applying the reactions postulated for the photo-oxidation of *N*-alkylamides to the polyamide chain, the remainder of the observed products of degradation can be accounted for. With oxidative attack occurring predominantly at the methylene group adjacent to the N atom, by reactions analogous to equations (12) to (15), subsequent decomposition of the derived alkoxy radical can occur as follows.



$$\begin{array}{c}\sim CO(CH_2)_4CO.NH\\ |\\ \sim NH(CH_2)_4CH_2.CH(O.)\end{array}\left|\begin{array}{l}\xrightarrow{X.}\begin{array}{r}\sim CO(CH_2)_4CO.NH\\ |\ +XH\\ \sim NH(CH_2)_4CH_2.CO\end{array}\qquad(25)\\ \longrightarrow\begin{array}{r}\sim CO(CH_2)_4CO.NH\\ |\\ \sim NH(CH_4)_2CH_2.+H.CO\end{array}\qquad(26)\\ \xrightarrow{XH}\begin{array}{r}\sim CO(CH_2)_4CO.NH\\ |\ +X.\\ \sim NH(CH_2)_4CH_2.CH.OH\end{array}\qquad(27)\end{array}\right.$$

$$\begin{array}{c}\sim CO(CH_2)_4CO.NH\\ |\\ \sim NH(CH_2)_4CH_3.CH.OH\end{array}\longrightarrow\begin{array}{c}\sim CO(CH_2)_4CO.NH_2\\ +\\ \sim NH(CH_2)_4CH_2.CHO\end{array}\qquad(28)$$

The reactions of equations (27) and (28) account for the observed production of aldehyde end-groups in the polymer, and of ammonia on hydrolysis of the corresponding amide end-groups formed. (The 6-aminohexanal which should also be produced on hydrolysis was not detected but may have been decomposed by the method of working up.) The reaction of equation (26) will also yield ammonia on hydrolysis together with formic acid and *n*-pentylamine. Though the presence of formic acid would be obscured by the acetic acid present, small amounts of *n*-pentyl amine (less than ten per cent of the total volatile bases) were detected. (By this reaction 10.6 nylon should yield *n*-nonylamine, and 6 nylon *n*-pentanoic acid which were in fact observed.) The alternative formation of pentylamine end-groups by photolysis of the aldehyde end-groups produced, may also occur to some extent.

Products from the reaction of equation (25) were not observed; the small amounts of 6-aminohexanoic acid to be expected on hydrolysis of photo-oxidized 6.6 nylon (or 9-aminononanoic acid from 10.6 nylon, or adipic acid from 6 nylon) were not distinguished in the complex pattern on the chromatogram. In fact their detection would not prove the occurrence of this reaction as the same products can arise by further oxidation of the aldehyde end-groups produced; this undoubtedly occurs and must account for much of the observed increase in carboxyl end-groups in the polymer.

Although these reactions are probably the predominant ones occurring in the photodegradation of polyamides, they are not the only ones. Thus hydrolysis of degraded 6.6 nylon resulted in the formation of small amounts of carbon monoxide and dioxide which probably arise by decomposition of hydroxy- or keto-acids; in addition small amounts of glutaric and succinic acids were detected. The formation of these compounds requires some oxidation to occur in the acid segment of the polyamide chain. Also the overall increase of u.v. absorption of 6.6 nylon on exposure to sunlight (*Figure 1*) is indicative of the formation of more complex groupings than those derived from the reactions described above. Discussion of these reactions has been based on the assumption, for example, that 6.6 nylon is pure polyhexamethyleneadipamide. In fact other uncharacterized groupings, associated with the absorption band at 2 800 to 2 900 Å[32], are introduced to a slight extent during manufacture by the thermal processes of polymerization and spinning. It is possible that these groupings influence the photodegradation by serving as absorbers of radiation and may provide the radical initiators required for the processes of degradation outlined above; they act as photosensitizers in increasing what, in their absence, would be a much slower reaction.

The effect of delustrant—The presence of titanium dioxide as delustrant in nylon polymer enhances the photodegradation only above 3 000 Å in the presence of oxygen and hence is connected with the photo-oxidation rather than the photolysis. No difference in chemical constitution was detected between photodegraded bright and delustred yarns. Although the rate of degradation of delustred yarns was much greater than bright, *Figures 2* to *10* indicate that relatively more chemical change occurred in bright than in delustred yarn for the same loss of tenacity. Presumably the enhanced degradation is confined to the locality of the titanium dioxide particles, and is more effective in causing tenacity loss than an equivalent amount spread more evenly as with bright yarn. The titanium dioxide thus does not appear to change the nature of the oxidation processes, but acts as a photo-sensitizer. From the practical point of view it is of considerable importance that certain additives, in particular manganous salts[16], have been found effective in limiting this photocatalytic action, and such additives are normally to be found in many delustred commercial nylon yarns.

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