Wet Oxidation of Undrawn Nylon 66 and Model Amides

E. MIKOLAJEWSKI, J. E. SWALLOW, and M. W. WEBB, *Royal Aircraft Establishment, Farnborough, Hampshire, England*

Synopsis

Undrawn nylon was found to be susceptible within a few days to degradation in wet or humid conditions at temperatures between 50 and 90°C. Model *N*-substituted amides, although not affected by these conditions, were attacked by hydrogen peroxide solutions. The degradation proceeded principally by rupture of the bond between the nitrogen of the amide and the carbon of its *α*-methylene group, consequent upon oxidation at this carbon. Unsubstituted primary amide, carboxyl, and aldehyde end-groups were formed, together with ammonia by hydrolysis of the oxidized amide. The bond between the *α* and *β* carbons of an *N*-methylene chain also suffered breakage, giving formic acid and carbon dioxide. The former could also arise by rupture of any initially produced *N*-formyl or *N*-formoyl amides. The appearance of lactic acid from butylacetamide showed that oxidation could proceed along the *N*-alkyl chain. Fragments of suitable size broken from the main chain of nylon became water-soluble and relatively stable to further attack by air or oxygen. These pieces essentially retained the nylon structure, but possessed two carboxylic ends and an average molecular weight of less than 600. A maximum oxygen uptake of about 30 moles per mole of original amide was calculated, corresponding to complete conversion into these soluble fragments. Significant degradation did not occur for many months at 60°C. in dry conditions or in solutions of 8-hydroxyquinoline, a process which has been patented. The latter was considered to function by chelating heavy metals into an inactive form and inhibiting peroxide formation.

INTRODUCTION

The partially drawn filaments commonly termed "undrawn nylon" produced in the first stage of the spinning of molten hexamethylene adipamide polymer possess a very high and largely irreversible extensibility. The property of absorbing large quantities of energy by converting work into heat has been used in a number of practical devices, for example, in emergency arrester gear on aircraft carriers. Unfortunately, it has been found that undrawn nylon, particularly when wet, undergoes degradation and loses its power to absorb energy. Badly affected portions of the nylon are yellow and brittle, strength and elongation may be nil, solution viscosity is low and a strong odor of degradation is apparent.

This report describes an investigation into the causes of the interesting and unexpected deterioration in properties, and a commercially acceptable method for inhibiting the breakdown is proposed.

MATERIALS

The following four samples of nylon were examined: (A) new undrawn ropes of 2 in. circumference. (Some tests were made on unserviceable returned ropes of the same construction.); (B) new undrawn singles yarn as used for constructing the 2-in. ropes; (C) material dating from 1956 in the form of undrawn ropes of $2^1/_2$ in. circumference; (D) drawn nylon cordage complying with British aircraft material specification DTD 481C, Cord no. 5. Further details of these samples are given in Appendix I.

The following four model amides were studied: N-methylacetamide, $CH_3CONHCH_3$; N-n-butylacetamide, $CH_3CONHC_4H_9$; acetamide, CH_3CONH_2; N,N-dimethylacetamide, $CH_3CON(CH_3)_2$.

N-Methylacetamide and N-n-butylacetamide contained all the types of linkage by which the nylon chain could be ruptured. The bond energy[1] of C—C links is 82.6 kcal./mole, compared with 72.8 kcal. for C—N links. Acetamide and N,N-dimethylacetamide were included to observe the effects of N-substitution. All the model amides were soluble in water, giving clear, colorless and odorless solutions.

EXPERIMENTS AND RESULTS

Effects of Various Environments on Yarn Strength

Air, Water, and Hydrogen Peroxide

Yarns were immersed in distilled water contained in jars placed in ovens at various temperatures. The changes in tenacity of sample A are shown in Figure 1. Water temperatures above 40°C. led within 10 days to a marked loss of strength and extension. The apparently anomalous transposition of the curves at 50 and 60°C. is probably of no significance.

At 100°C. the rate of degradation was less than at any temperature between 40 and 90°C., presumably as a result of the greatly reduced oxygen pressure in water at the boil. Yellowing did, however, occur in these conditions, indicating that the degree of coloration was not necessarily an index of the extent of the degradation and did not depend entirely on oxygen for its formation. Support for this was given by the fact that dilute hydrogen peroxide at 60°C. developed color in nylon relatively slowly. This might be taken as an indication that the color was not caused by a reaction between titanium dioxide (present in the fibers to act as delustrant) and oxygen to yield a peroxytitanic acid. The yellow color was not discharged by reducing agents such as sodium dithionite, nor could it be extracted by solvents. Its permanence might be attributed to a polymeric or an inorganic chromophore.

Drawing of the 2-in. rope yarns (sample A) by 100% did not appreciably slow the degradation in water at 60°C., but drawing by 200% decreased the rate considerably (Table I). Drawn yarn (sample D) suffered no significant loss in strength in 100 days immersion in water at 60°C. This

effect must result from the closer packing of the chain molecules following orientation by drawing, and is related to the slower rate of dye uptake (1:400) by drawn, as compared with undrawn, nylon. The difference is similarly manifested by the rates of methoxymethylation[2] of the two states of nylon.
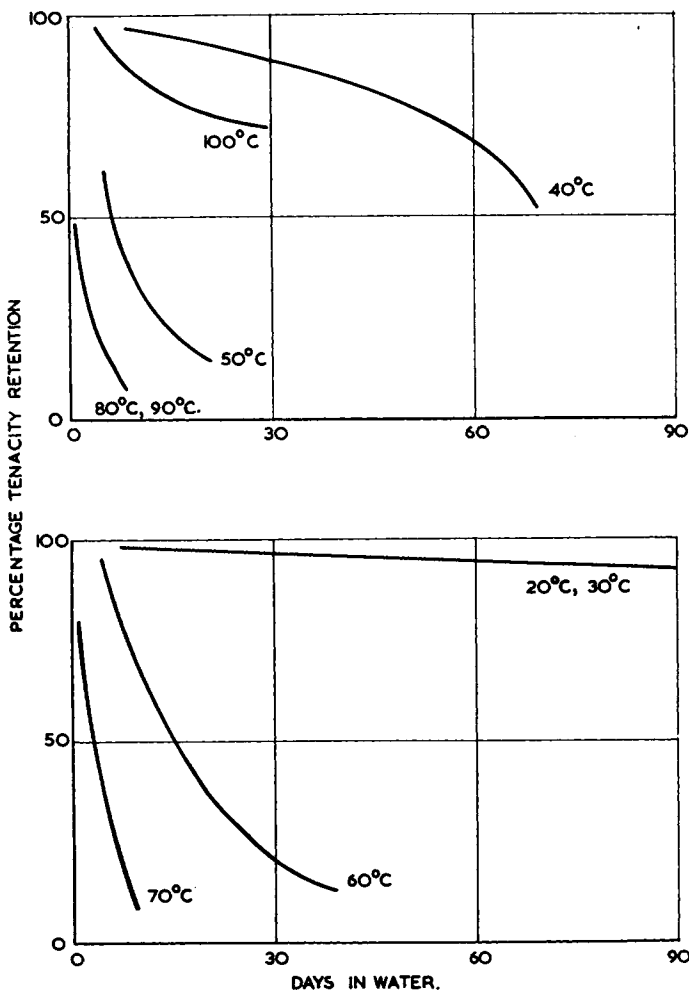

Fig. 1. Effect of distilled water at various temperatures on tenacity of undrawn nylon.

The conversion of singles yarn into rope did not introduce harmful new chemical factors, such as contamination by inorganic catalysts, since sample B degraded at a rate similar to sample A.

Water buffered at pH values of 6, 7, and 8 and air at high relative humidity (80%) caused damage in sample A at 60°C. comparable to unbuffered distilled water at 60°C. (Table II).

TABLE I

Effect of Temperature and Conditions on the Tenacity Retention of Various Types of Nylon

Material	Temperature, °C.	Environment	Tenacity retention after various times, %				
			5 days	10 days	20 days	50 days	100 days
A (2 in. circumference rope yarns)	20	1% H_2O_2	100	100	95	75	
	20	3% H_2O_2	95	95	95	50	
	20	10% H_2O_2	100	100	95	50	
	20	30% H_2O_2	95	95	85	70	
	100	3% H_2O_2	0				
	60	Drawn by 100%; transferred to water	70	50	35		
	60	Drawn by 200%; transferred to water	100	100	100	80	
B (Bobbin undrawn yarn, determined as percentage extension retention)	60	Water	25	0			
C (2½ in. circumference rope)	60	Water	100	100	100	100	85
	60	10% H_2O_2	85	30			
	60	1% $FeCl_3$	65	60	60	50	
D (DTD 481C yarns)	60	Water	100	100	100	100	100
	60	1% ferric chloride	90	80	55		
	60	1% ferric acetate	85	85	70		

The rate of degradation of all the samples in water was increased by replacing air with oxygen or water by hydrogen peroxide, particularly in the presence of iron salts (Tables I and II).

Sample C in water at 60°C. did not lose strength quickly, but in hydrogen peroxide solutions behaved similarly to sample A (Table I).

TABLE II

Tenacity Retention of 2-in. Rope Yarns at 60°C. in Various Environments

Environment	Tenacity retention after various times, %						
	5 days	10 days	20 days	50 days	100 days	200 days	500 days
Air, 10% R.H.	100	100	100	100	100	95	80
Air, 80% R.H.	80	65	55				
pH 6 buffer	100	95	40				
pH 7 buffer	100	85	40				
pH 8 buffer	100	85	50				
1% H_2O_2 (initial)	85	50	20				
3% H_2O_2 (initial)	80	40	0				
10% H_2O_2 (initial)	75	55	0				
30% H_2O_2 (initial)	45	10	0				
Oxygen in water	50	20					
Treated with 10% H_2O_2 at 20°C. for 4 days; transferred to water at 60°C. after washing	80	70	45				

Salts and Acids

Sample A which was susceptible to degradation in water did not degrade in 14 weeks at 60°C. in saturated sodium chloride solution (Table III). Concentrated salt solutions have been observed[3] to protect wool from the

TABLE III

Effect of Salts and Acids at 60°C. on Tenacity Retention of Yarns

Environment	Tenacity retention after various times, %				
	5 days	10 days	20 days	50 days	100 days
Saturated NaCl solution	100	100	100	100	100
5% NaCl solution	100	100	100	100	100
1% NaCl solution	100	95	55	40	
1% HCl solution	65	55	45		
1% HCl in saturated NaCl	40	30			

action of oxidizing agents.   The effect might result from the following factors, but a full investigation has not been carried out: (*a*) decreased solubility of oxygen in salt solutions; (*b*) decreased swelling of nylon by water in the presence of salt; (*c*) association of Na$^+$ and Cl$^-$ ions at CO—NH

TABLE IV

Effect of Inhibitors on the Tenacity Retention of Yarns

Inhibitor	Tenacity retention after various times at 60°C., %						
	5 days	10 days	20 days	50 days	100 days	200 days	500 days
10% sodium dithionite	100	100	100	100			
1% sodium dithionite	100	100	100	100			
0.1% sodium dithionite	100	100	60	30			
Treated with water 1 day at 60°C.; transferred to 10% sodium dithionite	95	95	95	90			
Treated with 10% sodium dithionite 1 day at 60°C.; washed and transferred to water	100	100	100	100	85	70	
Treated with 10% sodium dithionite 1 day at 60°C.; washed and transferred to 1% ferric acetate	70	55	30				
Saturated oxine in water	100	100	100	100	100	100	
Treated with saturated oxine 1 day at 60°C.; washed and transferred to water	100	100	100	100	100	100	100
Treated with saturated oxine 1 day at 60°C.; washed and transferred to 1% $FeCl_3$	95	85	75				
Treated with saturated oxine 1 day at 60°C.; transferred to 3% H_2O_2 without washing	100	80	10				
Treated with water 1 day at 60°C.; transferred to saturated oxine	95	95	95	95			
Treated with water 2 days at 60°C.; transferred to saturated oxine	95	95	95	95			

saturated oxine						
Treated with water 4 days at 60°C.; transferred to saturated oxine	95	95	80	80		
Treated with water 5 days at 60°C.; transferred to saturated oxine	65	65	65	55		
Treated with water 6 days at 60°C.; transferred to saturated oxine	50	50	50			
Treated with saturated oxine 1 day at 60°C.; transferred to water and oxygen bubbled continuously	100	100	100	100		
Treated with oxine solution in acetone; transferred to water	100	100	100	100	100	
Treated with saturated oxine in water 1 day at 60°C.; washed and transferred to water containing anatase TiO_2	100	100	100	100	100	
Treated with 10% H_2O_2 at 20°C. for 4 days; washed and transferred to saturated oxine	100	100	100	100	100	100
0.25% 1:10 phenanthroline in water at 60°C.	100	100	85	75	65	
Bobbin yarn (sample B) in saturated oxine at 60°C.	100	100	100			
Bobbin yarn (sample B) treated 1 day at 60°C. with saturated oxine; transferred to water at 60°C.	100	100	100			

dipoles, leading to decreased reactivity of the group or to a decrease in trace metal coordination; (d) inhibition of the formation of peroxides.

Sodium chloride did not inhibit the breakdown of nylon by hydrochloric acid solutions, but rather accelerated it. A similar phenomenon has been observed[4] in the weakening of silk finished in acid conditions.

Inhibitors

Table IV shows that solutions of sodium dithionite were effective in preventing degradation. Very dilute solutions quickly lost their power because of oxidation in the air, and sample A yarns withdrawn from concentrated solutions became weakened after immersion in water at 60°C. for three months.

TABLE V
Effect of Metallic Catalysts on the Tenacity Retention of Yarns

Catalyst	Tenacity retention after various times, %			
	5 days	10 days	20 days	50 days
Fenton's reagent at 20°C. (3% H₂O₂/ 1% FeSO₄)	55	50		
3% H₂O₂/1% ferric acetate at 20°C.	100	65	40	
Treated 1 day in 1% ferric acetate; transferred to 3% H₂O₂ at 20°C.	100	60	35	
1% ferric chloride at 60°C.	80	60	50	
3% ferrous sulfate at 60°C.	100	90	85	75
23% potassium oxalate	100	100	100	100
23% ferrous oxalate	100	90	60	
1 day in ferric acetate at 20°C.; transferred to 3% H₂O₂ at 60°C.	0			

A saturated aqueous solution of 8-hydroxyquinoline was an effective inhibitor, no significant weakening of yarns being apparent after 500 days (Table IV). When yarns which had been partially degraded in water for up to 6 days were transferred to oxine solution, further degradation was stopped or retarded. Oxine-treated nylon was resistant to degradation at 60°C. in water, 0.1N formic acid, anatase titanium dioxide (grade LF, trademark of British Titan Products Ltd.) suspensions and oxygen, but was not resistant to hydrogen peroxide, solutions of ferric salts or titanic acid at 60°C., or 0.1N formic acid at 100°C.

The oxine treatment has been commercially accepted and the process has been patented.

Catalysts

At 20°C. degradation by Fenton's reagent was more rapid than by either ferrous sulfate or hydrogen peroxide solutions alone (Table V).

Immersion in ferric salt solutions did not appreciably accelerate the loss in strength of untreated undrawn nylon in water, but pretreatment with

ferric salts increased the degradation of yarns immersed in hydrogen per-
oxide.   Samples C and D were both attacked by solutions of ferric salts at
60°C., being degraded at rates similar to that of sample A.   A similar
deleterious effect by iron salts or by rust on nylon and silk has been de-
scribed by several authors.

The iron and ash contents of three different ropes returned from an un-
serviceable pack are given in Table VI, together with results from samples
A, B, and C.   The ash consisted largely of anatase titanium dioxide.   The

TABLE VI
Iron and Ash Contents of Undrawn Nylon

Material	Iron content, ppm	Ash, %
Returned rope		
Badly degraded	45	0.41
Slightly degraded	53	0.45
Not degraded	43	0.44
Sample A	18	0.29
Sample B	18	0.29
Sample C	25	0.043

returned ropes had higher contents of iron and ash, but the quantity of iron
did not appear to be related to the extent of degradation.   Before analysis
the new yarns were desized by immersing in water at 60°C. for 24 hr.
Desizing was not practicable with the returned material.   The ash content
was determined by burning a known weight of nylon, and the iron esti-
mated in the residue by the colorimetric method of Brown and Hayes[5] with
1:10 phenanthroline.

Reynolds and Weiss[6] showed by studying the ultraviolet spectra of solu-
tions of ferric chloride in anhydrous N-methylacetamide that a complex ion
could be formed in the equilibrium (1).

$$Fe^{3+} + CH_3CONHCH_3 \rightleftharpoons CH_3CONFe^{2+}CH_3 + H^+ \tag{1}$$

Mixing of solutions of nylon and ferric chloride in formic acid gave a
greenish precipitate from which ferric chloride could be extracted by water
to restore the solubility of the nylon in formic acid.   With ferrous chloride
(obtained by dissolving iron in hydrochloric acid) no precipitate was ob-
tained with nylon solutions, but oxidation of the ferrous chloride, slowly in
the air or very rapidly with hydrogen peroxide, caused precipitation of the
complex.

Nylon therefore seemed to possess some slight affinity for ferric ions which
was probably essentially similar to that of the simple N-alkyl amides.

Hydrolysis

Hydrolysis of the N-alkyl substituted amide group in nylon was negligi-
ble at 60°C.   The number of amine endgroups, in fact, decreased slightly.
In boiling water, the carboxyl and amine ends increased only slowly in

number, and the tenacity decreased gradually (Fig. 1).   The deactivating effects of C and N substitution, combined with the low mass effect of H_2O because of phase difference render it unlikely on theoretical grounds[7] that hydrolysis alone could account for the observed degradation.

Solutions of $0.1N$ formic acid at 60°C. did not decrease the strength of yarns in an atmosphere of nitrogen, nor in air of yarns treated with oxine (Table VII).   Yarns immersed in boiling $0.1N$ formic acid, did, however, suffer losses of strength, and in these conditions hydrolysis of the amide linkage was significant.

TABLE VII
Effect of Hydrolysis on the Tenacity Retention of Yarns

	Tenacity retention after various times, %			
Conditions	5 days	10 days	20 days	50 days
$0.1N$ formic acid at 60°C. in atmosphere of nitrogen	100	100	100	
$0.1N$ formic acid at 100°C.	85	70	40	
Treated with saturated oxine 1 day at 60°C.; transferred to $0.1N$ formic acid at 100°C.	80	70	40	
Treated with saturated oxine 1 day at 60°C.; washed and transferred to $0.1N$ formic acid at 60°C.	100	100	100	100

Hydrolysis of the oxidation products was of great importance and is discussed further below.

Absorption of Oxygen by Nylon

The absorption of oxygen from air or an atmosphere of oxygen provided from a cylinder was measured by means of the apparatus illustrated in Figure 2.   This was a constant pressure respirometer modified by the incorporation of reflux condensers.   The undrawn nylon sample A was immersed in distilled water in flask A and an equal volume of distilled water was placed in the compensating vessel C.   When the atmosphere was to be of oxygen, air was boiled out from the water, and the system was saturated with oxygen by bubbling the gas through the water for 1 hr., the nylon being added when the temperature had fallen to 60°C.   The flasks were immersed in a large water-bath maintained at 60°C. by precise thermostatic control. At thermal equilibrium the polyvinyl chloride tubes T_1 and T_2 were sealed, and an arbitrary zero reading taken by observing the volume in the buret B.   Further readings of the volume in B after reducing the pressure differential in the manometer M to zero by altering the position of tube D gave the volume of gas absorbed in A, measured at the controlled ambient temperature (20°C.) of B and the barometric pressure at the time of sealing. This volume was reduced to dryness and standard temperature and pressure by the use of tables.
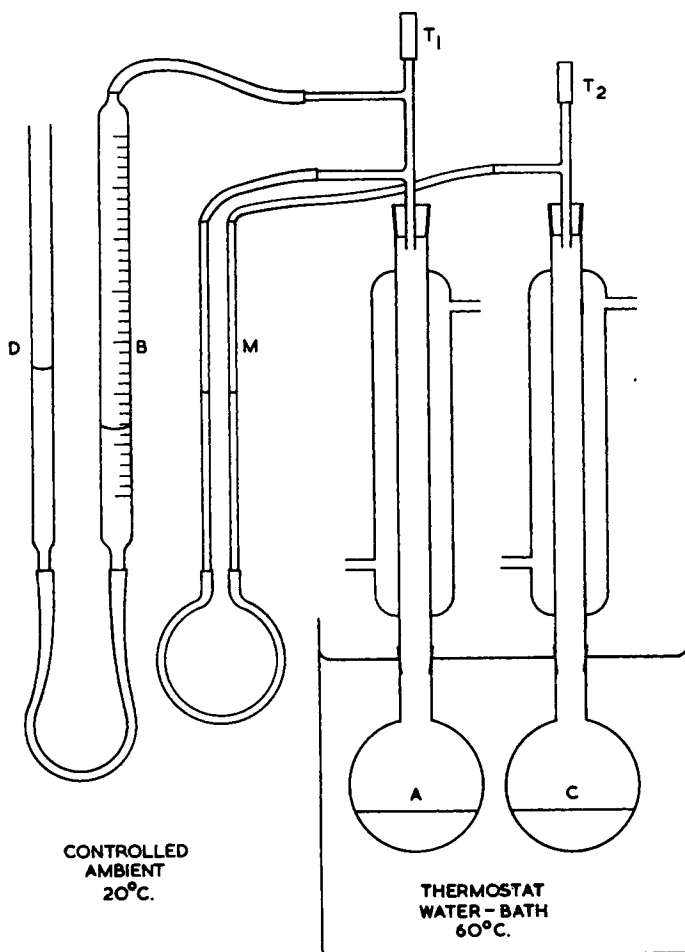
Fig. 2. Oxygen absorption apparatus.

Because of the small filament radius (1.7×10^{-3} cm.), the rate of diffusion of oxygen into the nylon should be considerable compared with the rate of reaction. It was therefore assumed that diffusion did not significantly influence the rate of oxidation.

The absorption of oxygen from air is shown in Figure 3. No apparent increase in the rate of absorption occurred after replenishing the air at point H, indicating that the oxygen partial pressure had not been reduced significantly.

The absorption of oxygen from an atmosphere of oxygen is shown in Figure 4. Results were corrected for oxygen wastage by trial runs without nylon.

In Figures 3 and 4, there is some resemblance to curves which have been obtained in the oxidation of heated nylon plastics and other polymers.[8] The data may be reduced to linear form by relating the rate of oxygen ab-

sorption to the logarithm of the amount of absorption (Figs. 5 and 6).   If Q
is the number of moles of oxygen taken up by 10^4 g. (molecular weight in
grams) of nylon in time t hours, the empirical eq. (2) is obeyed over the

$$dQ/dt = p - k \log Q \qquad (2)$$
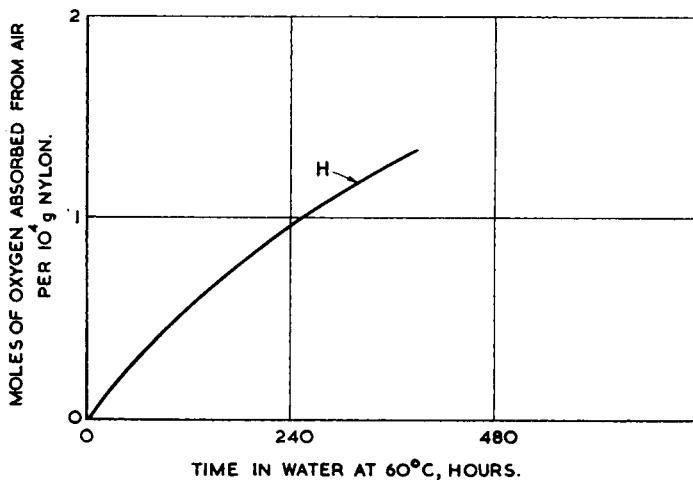
Fig. 3. Absorption of oxygen from air by undrawn nylon in water at 60°C.   Air supply
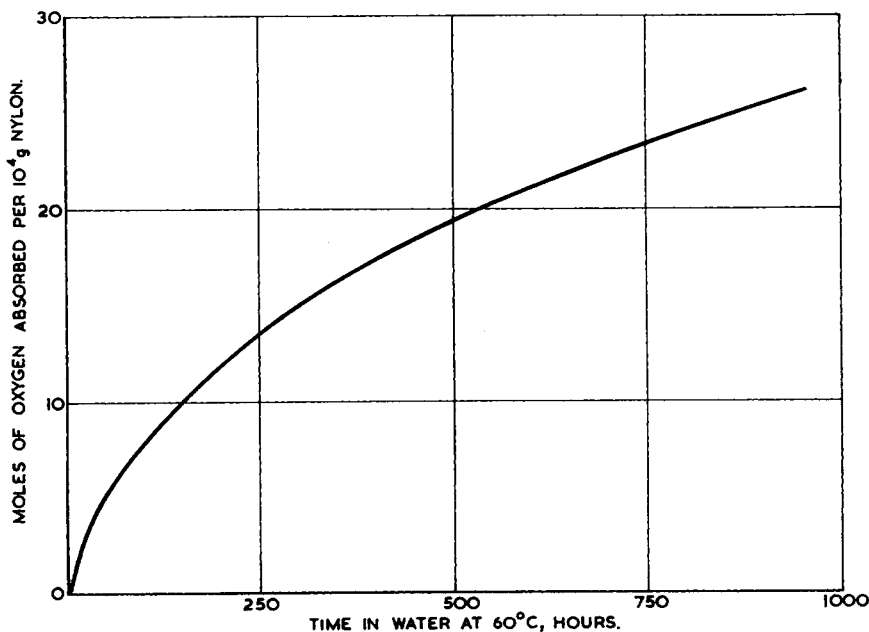replenished at point H.

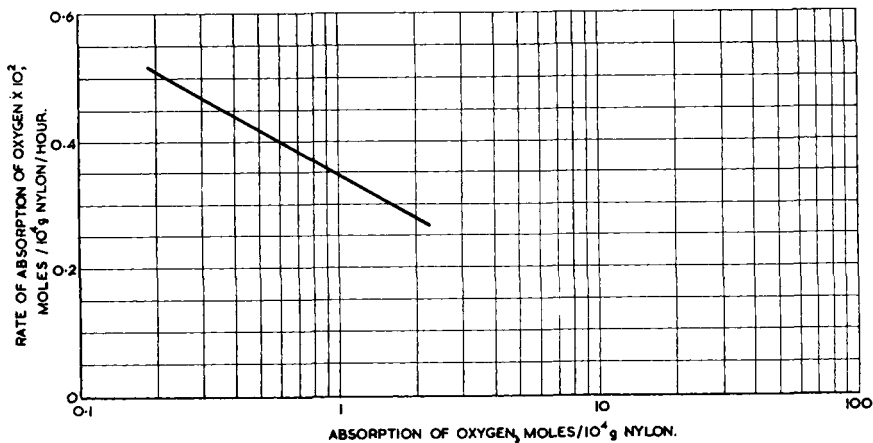Fig. 4. Absorption of oxygen from atmosphere of oxygen by undrawn nylon in water at
60°C.

Fig. 5. Rate of absorption of oxygen from air by undrawn nylon in water at 60°C.
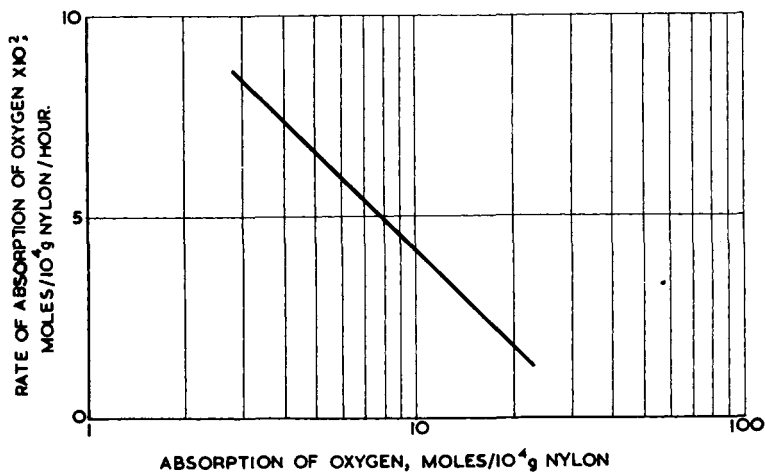
Fig. 6. Rate of absorption of oxygen from atmosphere of oxygen by undrawn nylon in water at 60°C.

range of the observations, and the constants p and k have different values for air and oxygen.

If extrapolation in Figures 5 and 6 can be extended to zero rate, a maximum oxygen uptake of about 30 moles by 10^4 g. of original nylon is indicated from both air and oxygen.

If the reaction between nylon and oxygen is expressed in the form

$$\text{nylon} + n\ O_2 \xrightarrow{v} \text{products} \tag{3}$$
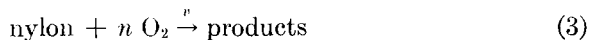
where v is the velocity of the rate-controlling step, then

$$v = a[\text{nylon}]\ [O_2]^n \tag{4}$$

where a is a constant.

Taking the rate of reaction to be $v = dQ/dt$, and assuming that the oxygen pressure remains constant, we may write eq. (4)

$$dQ/dt = b[\text{nylon}]$$

where

$$b = a[O_2]^n = \text{constant} \tag{5}$$

Hence

$$dQ/dt = b(1 - \alpha)$$

where α is the molar fraction of nylon which has reacted, so that

$$dQ/dt = b(1 - cQ) \tag{6}$$

if α is proportional to the oxygen uptake and c is a constant.

Integrating eq. (6) and putting $Q = 0$ when $t = 0$ gives

$$Q = (1/c)(1 - \exp\{-bct\}). \tag{7}$$

If we let the value of Q when $t = \infty$ be Q_∞, then $Q_\infty = 1/c$. If it is assumed that c and Q_∞ have the same values for the oxidation of nylon by both air and oxygen, then from Figures 5 and 6 a mean value of Q_∞ can be taken as 32 and $c = 3.12 \times 10^{-2}$.

By substituting values of t and Q taken from Figures 3 and 4 into eq. (7), the mean value of b was found to be 4.5×10^{-3} for oxidation by air and 6.1×10^{-2} for oxidation by oxygen. Hence the ratio $b_{\text{oxygen}}/b_{\text{air}} = 13.5$. Taking the partial pressure of oxygen in the air to be 0.21 atm. and substituting in eq. (5) gave $n = 1.7$. This value was not very sensitive to changes in the estimate of c or to variations of Q and t, within the limits of the experimental observations.

Chemical Examination of the Products of Degradation

Products of Soxhlet Extraction

Soxhlet extraction of undrawn nylon by water over a period of months, the temperature of the wet nylon being of the order 70–80°C., showed that low polymer of acidic character and fairly constant composition was continuously produced. The pH of the water extract was 7 initially, had fallen to 6 by the fourth day and to 4 by the eleventh day, thereafter remaining constant. The solutions gradually became yellow in color, and evaporation of the extract gave at first a white and later a yellow residue.

The weighed residues were redissolved in water as far as possible and titrated with $0.01N$/sodium hydroxide solution, bromothymol blue being used as indicator. The rates of extraction of solid matter and the development of acidity are shown in Figures 7a and 7b. From the slope of the curve in Figure 7b, the acid equivalent (i.e., the weight neutralized by 1 liter of normal sodium hydroxide) of the evaporated extract was calculated (Fig. 8). After the initial neutral extract consisting mainly of size, finishes, and low molecular weight polymer, the equivalent fell to 400 and later to 300.
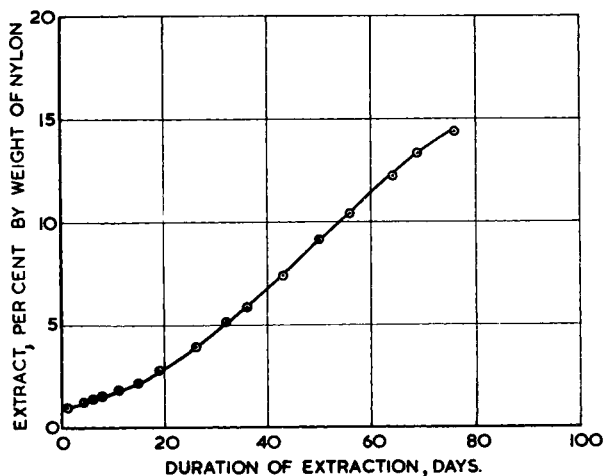
(a). RATE OF EXTRACTION.
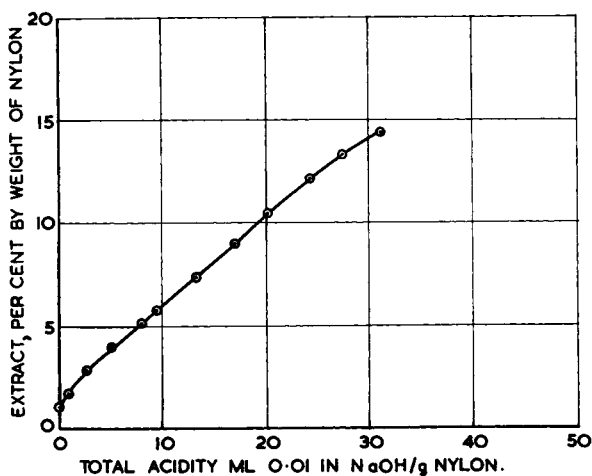
(b). DEVELOPMENT OF ACIDITY.

Fig. 7. Aqueous extraction of undrawn nylon at 70–80°C.

From Figure 7a, the steady rate of weight loss was about 0.2%/day or 2.3 × 10^{-11} g. nylon/sec. for each square centimeter of fiber surface at 70–80°C., or about 10^{-11} g./cm.² sec. at 60°C. This is comparable with the value of 3 × 10^{-12} g./cm.² sec. which may be taken as the average rate of oxygen uptake dQ/dt from air and water at 60°C., calculated from Figure 3.

The water extract (compound I) had the following percentage analysis by weight: C, 56.3%; H, 8.7%; N, 9.3%; 0, 25.7%. This corresponded to the composition I
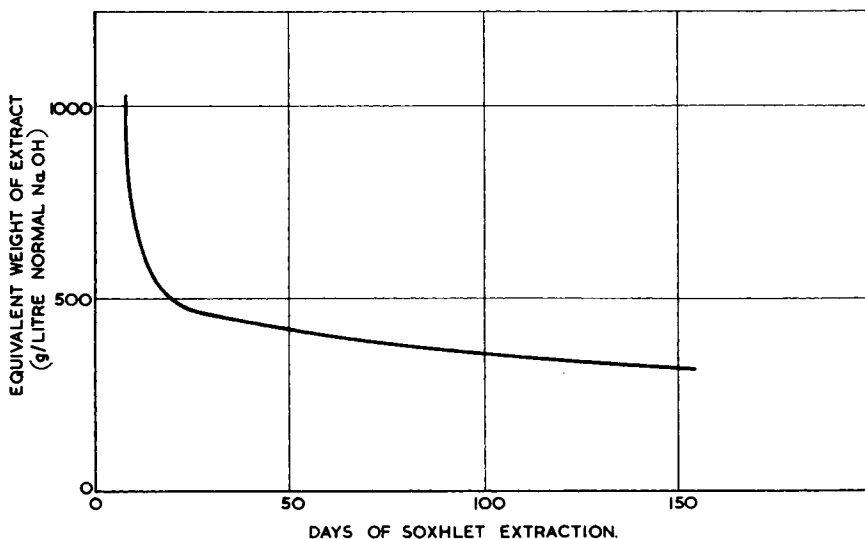
$$C_{7.02}H_{13.1}N\ O_{2.43}$$
I
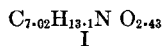
Fig. 8. Equivalent weight of Soxhlet extract.

In comparison with the original nylon ($C_6H_{11}NO$), the O:C ratio was increased and the N:C ratio decreased. The H:C ratio remained approximately constant. This material had 29.4 moles of COOH groups per 10^4 g. nylon, or 1 mole end in 340 g., and 3.5 moles of NH_2 ends per 10^4 g. The infrared spectrum of compound I is discussed below.

Analysis of Degradation Products

The formation of products from nylon was studied by refluxing at 60°C. with water or solutions of hydrogen peroxide. Qualitative analyses[9] for groups and compounds were made and those found in significant amounts were determined quantitatively by the methods described in Appendix II. Selected properties were examined at intervals, or more complete analyses were made at the conclusion of the tests.

The most rapid and consistent results with nylon were achieved with the use of oxygen from a cylinder as gas phase. In air the degradation was slower. Hydrogen peroxide solutions changed concentration continuously, making results difficult to interpret.

Analyses of the degradation products from nylon and oxygen are given in Table VIII.

Hydrogen peroxide was detectable within 1 hr. of bubbling oxygen through nylon in boiled-out water at 60°C. The concentration increased for approximately 3 days to a total of about 2 moles $H_2O_2/10^4$ g. nylon and then fell to zero within a month. No hydrogen peroxide was detected when air was used as the oxidant.

The equivalent weight of the nylon portion passing into solution, with oxygen as the gas phase, was almost constant at about 300. The corre-

TABLE VIII

Degradation Products from Undrawn Nylon in Water

Temperature, 60°C.; Time, 70 days; Oxidant, Cylinder Oxygen

Undissolved portion	
Carboxyl endgroups, moles/mole nylon[a]	4.0
Aldehyde endgroups, moles/mole nylon[a]	2
Amine endgroups, moles/mole nylon[a]	0.23
Ammonia after alkaline hydrolysis, moles/mole nylon[a]	1.7
Molecular weight (viscometric)	2,000
Molecular weight of original nylon	10,400
Elemental composition[b]	
Carbon, %	61.2
Hydrogen, %	9.9
Nitrogen, %	11.6
Oxygen (by difference), %	17.3
Water phase	
Soluble residue, % of original weight of nylon	7.3
Formic acid moles/mole nylon[a]	0.29
Ammonia, moles/mole nylon[a]	0.35
Ammonia after alkaline hydrolysis, moles/mole nylon[a]	1.7
Equivalent weight in solution	245
Equivalent weight after evaporation	267
Molecular weight (cryoscopic)	557
Aldehyde in solution, moles/mole nylon[a]	6.2
Aldehyde after evaporation	nil
Elemental composition[b]	
Carbon, %	53.3
Hydrogen, %	8.6
Nitrogen, %	9.3
Oxygen (by difference), %	28.8
Gas phase	
Carbon dioxide, moles/mole nylon[a]	1.75

[a] Expressed in moles of product per mole (10^4 g.) of original nylon.

[b] Theoretical composition of original nylon $(C_{12}H_{22}O_2N_2)_n$: C, 63.7%; H, 9.8%; N, 12.4%; O, 14.2%.

spondence between this figure and that from the Soxhlet extraction (compound I) was noteworthy and suggested that the water-soluble portion was fairly stable toward further chain scission by oxygen. The molecular weight, determined cryoscopically, was approximately 600, showing that there were two carboxyl ends in the average molecule. The lack of significant difference between the equivalent weight determined in solution and after evaporation (Table VIII) indicated that the dissolved aldehyde was volatile and was not converted into carboxyl on evaporation.

In solutions of hydrogen peroxide, chain scission of nylon proceeded further than for oxygen and water. For example after 10 weeks at 60°C. in 30% H_2O_2 (initially) the acid equivalent was reduced to 145.

Carboxyl and aldehyde endgroups of the undissolved nylon increased progressively with time, when calculated with reference to 10^4 g. of original nylon. For oxygen and water at 60°C. the rate of increase in the number of carboxyl groups, assumed to be linear though with considerable scatter,

was about 5×10^{-2} mole COOH/10^4 g. of original nylon per day, while aldehyde was produced at half this rate.   Molecular weight determinations showed that carboxyl and aldehyde together made up more than half of the new ends.

For air and water at 60°C. the rate of increase of carboxyl groups was approximately 5×10^{-3} mole/10^4 g. nylon per day.   In 6% hydrogen peroxide solution the rate was at first about the same as for oxygen and water; after 20 days the H_2O_2 concentration was much reduced and the rate became the same as for air and water.

Molecular weight was estimated by determining the viscosity at 25°C. of 1% solutions of nylon in 90% formic acid, by use of an Ubbelohde viscometer of narrower capillary than a No. 1, and applying eqs. (8) and (9):

$$[\eta] = (3/c)\,(\eta_r^{1/3} - 1) \tag{8}$$

$$\bar{M}_n = 13{,}000\,[\eta]^{1.39} \tag{9}$$

where $[\eta]$ is intrinsic viscosity, η_r = viscosity relative to the solvent (90% formic acid), c = percentage concentration (in grams/100 ml. solution), $\bar{M}_n$ = number-average molecular weight.   Many equations[10,11] have been suggested relating molecular weight and viscosity, but it cannot be assumed that nylon would follow the same viscosity–molecular weight relationship throughout its degradation.   Although Taylor's equation [eq.(9)] was derived with a viscometer giving rather short flow times, several authors have used it, and in the present investigation it was considered suitable for comparative purposes.

Carbon dioxide was evolved from undrawn nylon in oxygen and water at 60°C. at the linear rate of 2.5×10^{-2} mole/10^4 g. original nylon per day, comparable with the figure of 1.55×10^{-2} mole CO_2/mole per day calculated from data for malonic acid.[7]   The similarity suggested that carbon dioxide might be formed by decarboxylation of dicarboxylic acid.   Carbon dioxide would also arise by the reaction of formic acid with hydrogen peroxide.   In air and water at 60°C., the rate of formation of carbon dioxide was about 2×10^{-3} mole/10^4 g. nylon per day.

Hydrolysis of the oxidation products was responsible for the appearance of ammonia.   The amounts of free ammonia and formic acid in the water phase of the nylon degradation were rather variable, probably because of their volatility in a current of oxygen.

Degraded nylon gave a greatly increased pyrrole reaction with p-dimethylaminobenzaldehyde, although the molar proportion of pyrrole was still very small (about 30–50×10^{-4} mole/10^4 g. original nylon in comparison with about 1×10^{-4} mole in the original yarn).   A limit might be set to the quantity of detectable pyrrole at a certain degree of polymerization by a lack of new free CH groups in the α or β position as a result of crosslinking of pyrrole nuclei.   It is possible that the yellow color of degraded nylon could be accounted for by pyrrole polymer,[12] the appearance of which did not necessarily require oxygen.

Another color reaction given by degraded nylon was obtained by adding concentrated sulfuric acid to a solution in *m*-cresol, the intensity of the red color produced being roughly related to the extent of degradation.   Formic acid and formaldehyde gave an identical color, and it seems probable that formate or formyl groups[13] on the ruptured nylon chains were responsible for the reaction.

Physical Examination of Degraded Nylon

Infrared Spectra

Infrared spectra were obtained with a Perkin-Elmer Infracord spectro-photometer on disks pressed from a mixture of chopped and ground nylon with excess of dried potassium bromide.

The spectra of a badly degraded undrawn nylon (compound I from the Soxhlet extraction) and an undegraded undrawn nylon (sample A) are re-
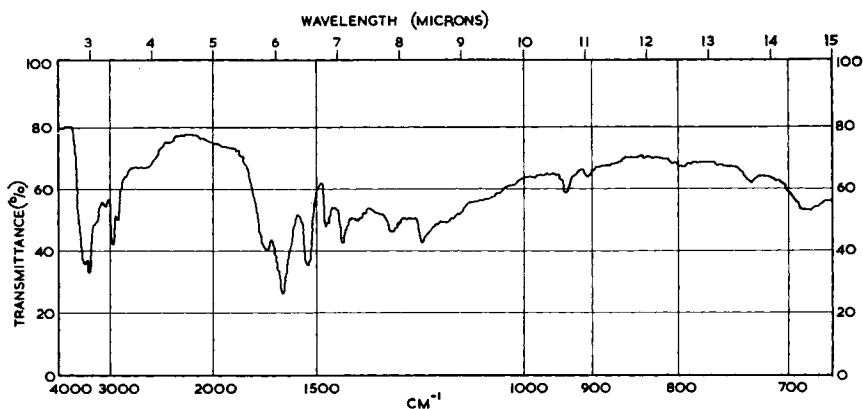
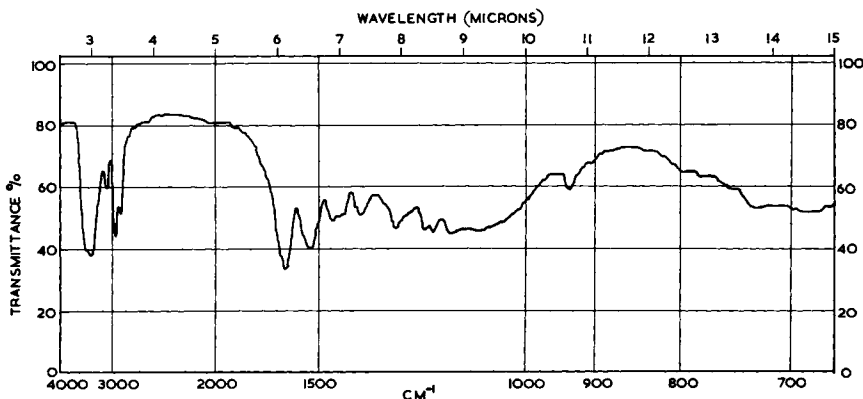Fig. 9. Infrared spectrum of a badly degraded undrawn nylon.

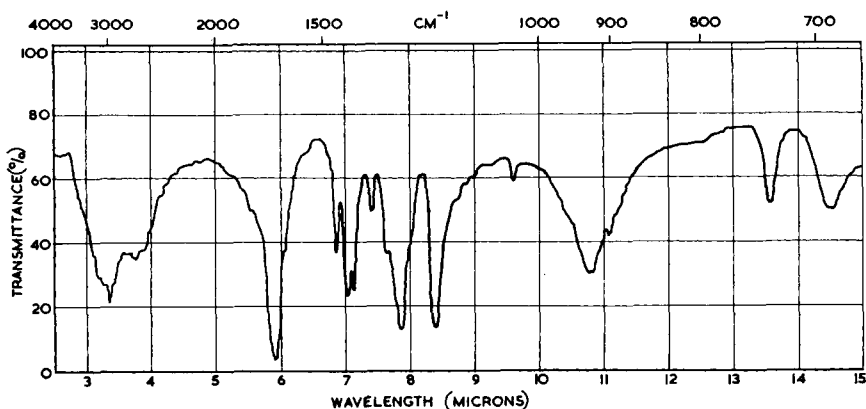Fig. 10. Infrared spectrum of undegraded undrawn nylon.

Fig. 11. Infrared spectrum of adipic acid.

produced in Figures 9 and 10.   The degraded nylon retained the characteristic nylon bands and in addition new or intensified peaks appeared, attributable[14] to CO-containing groups, principally carboxyl and aldehyde. The spectrum of adipic acid (Fig. 11) superposed on that of undegraded nylon could largely account qualitatively for the spectrum of the degraded material, except for two small bands in some samples at frequencies of 1060 and 1470 cm.$^{-1}$, for which no explanation can be given.   Bands characteristic of peroxide groups were not detected in any of the nylon samples examined.   Absence of new bands attributable to amide III to the region of 1305–1200 cm.$^{-1}$ would seem to exclude secondary amide.

X-Ray Diffraction

An increase in the crystallinity of a polymer might be expected to lead to reduced chain extension or brittleness by restricting movement of the molecular chains.   The degree of crystallinity may be estimated from x-ray diffraction patterns by the sharpness and character of the rings and arcs.

X-ray fiber patterns were taken with the use of filtered CuKα radiation and a flat film 4 cm. from the specimens.   The photographs are shown in Figure 12a from an undegraded yarn and Figure 12b from a badly degraded sample.

There appeared to be no significant difference between the patterns, indicating that the brittleness of the degraded sample could not be attributed to an increase in crystallinity.

Chemical Examination of Products of Degradation of Model Amides

The model amides, N-methylacetamide and N-butylacetamide, were not attacked in 21 days at 60°C. by molecular oxygen in water, even with ferric chloride present.   This result might depend on the lack of intimate contact between the amide and oxygen in dilute solution, or on the relative
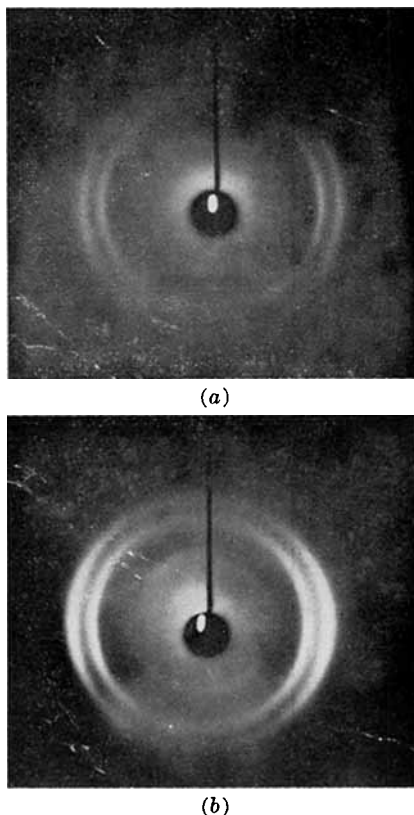
(a)

(b)

Fig. 12. X-ray diffraction photographs: (a) lightly degraded undrawn nylon; (b) badly degraded undrawn nylon.

inefficiency of ferric chloride as catalyst. Hydrogen peroxide solutions attacked the model amides, however, and so were used at 60°C. for work on oxidation, generally with ferric chloride present to accelerate the reaction and to decompose excess peroxide. No color was produced in the absence of ferric chloride, showing that the simple amide structure on oxidation was not sufficient to produce a chromophore.

In all cases of butylacetamide oxidation a slight butyric odor was evident, but there was no increase in acid titer or amine content after 10 days in water at 60°C. The reaction constants for the hydrolysis of a number of amides and peptides are given in the literature.[15] Simple amides hydrolyze fairly readily, but N-substituted amides hydrolyze more slowly, even when in homogeneous solution in the presence of carboxylic acids.[16] Since various amides and peptides have similar activation energies for hydrolysis, it is probable that they all hydrolyze by the same mechanism.

Analysis of the degradation products from methylacetamide and butylacetamide with hydrogen peroxide are given in Table IX. In closed conditions, more than 90% of the nitrogen was recovered as ammonia after

TABLE IX

Degradation Products from N-Methylacetamide and N-n-Butylacetamide

Amide	Molar ratio, available O$_2$:amide	Temp., °C.	Catalyst	Test time, days	Products, moles/mole original amide						
					Formic acid	Ammonia	Ammonia after hydrolysis	Acetaldehyde	Lactic acid	Amines (as butylamine)	Carbon dioxide
N-Methylacetamide	2.2	60	1% FeCl$_3$ (20 ml./100 ml. reaction mixture)	4	0.17	0.34	1.00	0.32	nil	nil	0.69
N-n-Butylacetamide	1.8	20	''	22	0.07	0.10	0.91	0.03	0.51	0.002	a
	3.2	20	''	203	0.12	0.32	0.97	0.20	0.47	0.002	a
	1.8	60	''	10	0.09	0.06	0.95	0.06	0.40	0.002	a
	3.6	60	''	7	0.14	0.34	0.85	0.06	0.39	0.002	a
	4.4	60	''	7	0.09	0.35	0.90	0.06	b	0.003	1.55
	4.4	60	None	21	0.03	0.56	0.88	b	b	0.002	0.24

a Not determined.

b Presence of undecomposed hydrogen peroxide interfered with estimation.

alkaline hydrolysis, indicating virtually complete oxidation of the original amide. Formic acid and carbon dioxide accounted for 0.9 of the methyl carbon of N-methylacetamide, while in N-n-butylacetamide, 3.1 of the butyl carbons gave rise to formic acid, lactic acid, and carbon dioxide. A large proportion of the carbon dioxide evolved from the model amides might be accounted for by the reaction of formic acid with hydrogen peroxide.

Oxidized butylacetamide also gave the color reaction with sulfuric acid and cresol noted with nylon above, and may be attributed to the same cause.

MECHANISM OF DEGRADATION

The production of formic acid by the reaction of hydrogen peroxide solutions with N-methylacetamide and N,N-dimethylacetamide, but not with acetamide, showed that the carbon atom adjacent to the nitrogen of N-substituted amides was susceptible to attack. More remote carbon atoms in an N-methylene chain would be less vulnerable, bearing in mind the relative strengths of C—C and C—N bonds, but the formation of lactic acid from N-n-butylacetamide showed that oxidation could proceed along the chain.

The almost quantitative yield of ammonia after alkaline hydrolysis of the oxidized model amides, and the absence of amines in significantly increased amounts, proved that nearly complete oxidation at the α carbon and breakage of the α C—N bond occurred before hydrolysis.

A number of metal ions, including titanium, can[17,18] to some extent catalyze the conversion of water into active free radicals and hydrogen peroxide. It is postulated that 8-hydroxyquinoline interferes with this conversion by sequestering the metallic ion. Attack on the amide radical $R^1CONH\dot{C}HR^2$ would follow the production of active radicals, leading to $R^1CONH\dot{C}H(O)$—. Rupture of the N—C bond and hydrolysis of the resulting amide would account for the appearance of ammonia. Acetaldehyde might arise in considerable quantities from methylacetamide as a result of the alternative decompositions of the amide $CH_3CONHCHO$.

The absence of reaction between oxygen and the model amides, even in the presence of ferric chloride, might be accounted for by the decay of the radicals before attack on the amide could occur.
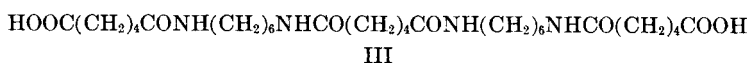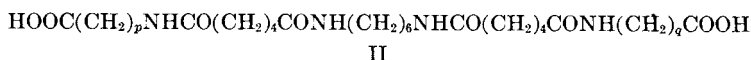
Resolution of origin of the oxidative oxygen might be achieved by the method of Brodski.[19] If water enriched in $H_2^{18}O$ were used for the oxidation of nylon, the mechanism outlined would lead to degradation products containing ^{18}O.

The α-methylenes of N-alkyl chains were not converted into stable carbonyl to any great extent, since butyric acid was not a major hydrolysis product of oxidized butylacetamide, nor was N-acetylbutyramide, $CH_3CONHCOC_3H_7$, isolated, as might have been expected in view of its slight solubility in water.

Rupture of C—C bonds, particularly the α–β bonds, by a free radical mechanism or as a result of decarboxylation, would give formyl endgroups,

formic acid, and carbon dioxide, together with carboxyl, aldehyde, or hydro-carbon endgroups.

The composition and properties of the water-soluble fragments of oxidized nylon suggested that as pieces of suitable size were broken from the main polymer they passed into solution and became relatively immune to further chain scission by oxygen. A mixture of water-soluble fragments was to be expected, since the chains were ruptured asymmetrically, but the average

$$HOOC(CH_2)_pNHCO(CH_2)_4CONH(CH_2)_6NHCO(CH_2)_4CONH(CH_2)_qCOOH$$
$$II$$

$$HOOC(CH_2)_4CONH(CH_2)_6NHCO(CH_2)_4CONH(CH_2)_6NHCO(CH_2)_4COOH$$
$$III$$

compounds II (where $p + q = 4$) and III were in reasonable accord with the data. As lactic acid was a product of butylacetamide oxidation, it was reasonable to conclude that the excess oxygen indicated by the elemental analysis of the water-soluble fragments was present in hydroxyl groups attached to the carbon chains.

APPENDIX I

Details of Nylon Samples

Sample A. Plied yarns extracted from the new ropes as received had the properties given in Table X.

TABLE X
Properties of Nylon Yarns

Property	Yarn A Mean	Standard deviation (SD)	Yarn B Mean	SD	Yarn C Mean	SD	Yarn D Mean	SD
No. of filaments (approx.)	200	—	10	—	136	—	360	—
Count, tex (g./km. length)	209	14	9.8	0.4	445	5	130	1
Breaking strength, kg.	2.2	0.3	—	—	3.6	0.2	5.6	0.14
Tenacity, g./tex (kg./mm.²/density)	10.6	0.8	—	—	8.2	0.4	43.8	1.2
Breaking extension, %	234	7	267	14	579	38	—	—
Filament diameter, μ	35	—	—	—	—	—	10	—
Delustrant (anatase titanium dioxide), %	0.3	—	—	—	0.04	—	0.3	—

Sample B. The yarn was the precursor of 30 den. (3.3 tex) medium tenacity drawn yarn (British Nylon Spinners Ltd. Type 100, semidull). The properties are given in Table X.

Sample C. The single yarn used was the precursor of 210 den. (23 tex) high tenacity drawn nylon (British Nylon Spinners Ltd. Type 300 bright). Plied yarns extracted from the rope had the properties given in Table X. The material was notable in having a very high extension and a low delustrant content; it was also interesting in possessing a greater resistance to wet degradation than semidull nylon.

Sample D. The properties of plied yarns extracted from the cord are given in Table X.

APPENDIX II

Quantitative Methods of Determining Degradation Products

The following products were examined using methods described in the cited references.

Hydrogen Peroxide. Hydrogen peroxide was determined colorimetrically with titanic acid or volumetrically with potassium iodide and standard sodium thiosulfate solution.

Ammonia. Ammonia, before and after alkaline hydrolysis of the oxidized product, was determined colorimetrically with Nessler solution.[20]

Formic Acid. Formic acid was determined colorimetrically with chromotropic acid.[20]

Carbon Dioxide. Carbon dioxide was determined gravimetrically by sweeping the system with CO_2-free oxygen and absorbing the dried CO_2 with soda–asbestos M.A.R.

Carboxyl Endgroups. Carboxyl endgroups were determined by titration with standard sodium hydroxide solution; benzyl alcohol was used as solvent for polymer and hydroxide when determining nylon insoluble in water.[12]

Amine Endgroups. Amine endgroups were determined by titrating nylon solutions in 90% phenol with standard hydrochloric acid;[12] in model amides, colorimetrically with picric acid.[20]

Aldehyde Endgroups. Aldehyde endgroups on nylon were determined colorimetrically with Schiff's reagent[20] in the water extract and with 2,4-dinitrophenylhydrazine[20] in the undissolved polymer.

Pyrrole. Pyrrole was determined colorimetrically with p-dimethylaminobenzaldehyde.[12]

Acetaldehyde. Acetaldehyde, was determined colorimetrically with Schiff's reagent.[20]

Lactic Acid. Lactic acid was determined colorimetrically with p-hydroxydiphenyl in sulfuric acid[20] and by subtracting the acetaldehyde determined.

Molecular Weight. Molecular weight was determined viscometrically in 90% formic acid by using Taylor's equation, or cryoscopically by using camphor.

Iron. Iron was determined by ashing and estimating colorimetrically with 1 : 10 phenanthroline.[5]

References

1. Cottrell, T. L., *The Strength of Chemical Bonds*, Butterworths, London, 1958.
2. Lewis, J. R., and R. J. H. Reynolds, *Chem. Ind. (London)*, **1951**, 958.
3. McPhee, J. R., *Textile Res. J.*, **30**, 349 (1960).
4. Howitt, F. O., Shirley Lecture Series No. 13 (1948).
5. Brown, E. G., and T. J. Hayes, *Anal. Chim. Acta*, **7**, 324 (1952).
6. Reynolds, W. L., and R. H. Weiss, *J. Am. Chem. Soc.*, **81**, 1790 (1959).
7. Schefer, W., *Textil Rundschau*, **10**, 279, 365, 423 (1955).
8. Grassie, N., *The Chemistry of High Polymer Degradation Processes*, Butterworths, London, 1956.
9. Feigl, F., *Spot Tests in Organic Analysis*, Elsevier, Amsterdam, 1956.
10. Pavlova, S. A., and S. R. Rafikov, *Vysokomol. Soedin.*, **1**, 387 (1959).
11. Heim, E., *Faserforsch. Textiltech.*, **11**, 513 (1960).
12. Rochas, P., and J. C. Martin, *Bull. Inst. Textile France*, No. 83, 41 (1959).
13. Henbest, H. B., and M. J. W. Stratford, *Chem. Ind. (London)*, **1961**, 1170.
14. Bellamy, L. J., *The Infra-red Spectra of Complex Molecules*, Methuen, London, 1958.
15. *Table of Chemical Kinetics*, National Bureau of Standards, Circular 510 (1951).
16. Wyness, K. G., *J. Chem. Soc.*, **1958**, 2934.
17. Dainton, F. S., *J. Chem. Soc.*, **1952**, 1533.
18. Cook, J. W., W. Carruthers, and W. A. Waters, *Progress in Organic Chemistry*, Vol. 5, Part 1, Butterworths, London, 1961.
19. Brodski, A. E., *Dokl. Akad. Nauk. USSR*, **123**, 117 (1958).
20. Snell, F. D., and C. T. Snell, *Colorimetric Methods of Analysis*, Van Nostrand, New York, 1953.

Résumé

On a trouvé que le nylon non-étiré était susceptible de subir en quelques jours une dégradation à l'état mouillé ou humide à des températures situées entre 50 et 90°C. Les amides N-substituées de référence, bien qu'elles ne soient pas affectées par ces conditions, sont attaquées par des solutions de peroxyde d'hydrogène. La dégradation se produit principalement par rupture de la liaison entre l'azote de l'amide et le carbone de son groupe méthylène en α, consécutif à l'oxydation de ce carbone. L'amide primaire non substituée ainsi que des groupes terminaux carboxyle et aldéhyde se forment, accompagnés d'ammoniac provenant de l'hydrolyse de l'amide oxydée. La liaison entre les carbones α et β d'une chaîne N-méthylène subit également la rupture en produisant de l'acide formique et de l'anhydride carbonique. Le premier peut également se former par rupture de chacun des amides N-formyl ou N-formoyl produits initialement, L'apparition d'acide lactique à partir de butylacétamide montre que l'oxydation peut se faire le long de la chaîne N-alcoyle. Des fragments de mixture de dimension convenable provenant de la chaîne principale du nylon deviennent solubles dans l'eau et relativement stable vis à vis d'une attaque ultérieure par l'air ou l'oxygène. Ces fragments conservent essentiellement la structure du nylon, mais possèdent deux groupement carboxyliques terminaux et un poids moléculaire moyen plus petit que 600. On a calculé qu'il fallait un maximum d'environ 30 môles d'oxygène par môle d'amide originel near obtenir une conversion complète en ces fragments solubles. Une dégradation marquée ne se produit pas pendant plusieurs mois à 60°C dans des conditions

sèches, ou en solution dans la 8-hydroxyquinoléine, procédé qui a été breveté. Cette dernière est considérée comme formant par chélation de métaux lourds une forme inactive et inhibitrice de formation de peroxyde.

Zusammenfassung

Ungerecktes Nylon zeigte innerhalb einiger Tage in nassem oder feuchten Zustand bei Temperaturen zwischen 50 und 90°C Abbauerscheinungen. N-substituierte Amide als Modellverbindungen wurden zwar unter diesen Bedingungen nicht angegriffen, wohl aber durch Wasserstoffperoxydlösungen. Der Abbau verlief hauptsächlich über eine Spaltung der Bindung zwischen dem Amidstickstoff und dem Kohlenstoff seiner α-Methylengruppe, welche auf eine Oxydation an diesem Kohlenstoff folgte. Unsubstituiertes primäres Amid, Carboxyl- sowie Aldehydendgruppen wurden zusammen mit Ammoniak gebildet, der aus der Hydrolyse des oxydierten Amides stammte. Auch die Bindung zwischen dem α- und β-Kohlenstoff einer N-Methylenkette wurde, und zwar unter Bildung von Ameisensäure und Kohlendioxyd, gespalten. Erstere Könnte auch durch Spaltung eines zuerst gebildeten N-Formyl- oder N-Formoylamids entstehen. Die Bildung von Milchsäure aus Butylacetamid zeigte, dass die Oxydation entlang der N-Alkylkette fortschreiten kann. Aus der Hauptkette von Nylon abgespaltene Bruchstücke von geeigneter Grösse waren wasserlöslich und gegen weiteren Angriff durch Luft oder Sauerstoff verhältnismässig beständig. Diese Bruchstücke besassen im wesentlichen Nylonstruktur und hatten zwei Carboxylendgruppen sowie ein mittleres Molekulargewicht kleiner als 600. Für eine vollständige Umwandlung in diese löslichen Bruchstücke wurde eine maximale Aufnahme von 30 Mol Sauerstoff durch ein Mol des ursprünglichen Amids berechnet. Bei 60°C unter trockenen Bedingungen oder in 8-Hydroxychinolinlösung, was patentiert wurde, trat durch viele Monate kein wesentlicher Abbau ein. Letzteres wurde durch Chelatbildung mit Schwermetallen zu einer inaktiven Form und Verhinderung der Peroxydbildung erklärt.