# Effects of Thermal Exposure on the Physicochemical Properties of Polyamides*

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## Synopsis

Nylon 66 and nylon 6 yarns were exposed in air, nitrogen, and vacuum to temperatures from 136 to 215°C. for periods from 5 min. to 17.5 hr.   The moisture absorption of both fibers is reduced by the exposure independently of the presence of oxygen or of antioxidant.   This is ascribed to secondary crystallization.   Simultaneously, the electrical resistivity is increased.   The breaking strength is reduced by exposure in the presence of oxygen unless the polymer contains antioxidant.   The extent of oxidative cleavage was measured by the viscosity-average molecular weight $\bar{M}_v$ of nylon 66.   Simultaneously, a reduction of the amine endgroup content was observed.   It occurs only in the presence of oxygen and approaches a limit indicating that some amine groups are not subject to elimination.   If oxygen is absent or the polymer protected by antioxidant, the $\bar{M}_v$ increases.   Sorption of hydrochloric acid is reduced by the exposure.   Only 80% of the amine groups in the unexposed and 55% in the exposed nylon participate in acid binding at pH 2.5.   The rate constants of cleavage as manifested by $\bar{M}_v$ and of the process leading to disappearance of amine groups were determined for nylon 66.   The activation energies were calculated 40 and 36 Kcal./mole, respectively.

## INTRODUCTION

Shortly after the commercial production of nylon began in 1938, it was reported that its dye absorption decreases on heat setting and that its mechanical properties deteriorate on prolonged exposure to heat in presence of air.   Until quite recently, the literature showed hardly any effort to characterize chemically these irreversible changes caused by exposure to elevated temperatures below the melting point of the polymer.   Our investigation commenced in 1958 to fill in the gaps, and some of the results were described in 1961 in a report of limited distribution.[1]

We exposed nylon 66 and nylon 6 yarns to temperatures between 136 and 215°C. for periods ranging from 5 min. to 17.5 hr., in air, as well as in vacuum and nitrogen.   In order to obtain insight into the nature of the structural changes, the following properties were measured as a function of

the exposure conditions: breaking strength and breaking elongation of yarn, equilibrium moisture absorption at 65% R.H. and 70°F., absorption of hydrochloric acid from aqueous solution, amino group content, carboxyl group content, and viscosity-average molecular weight.

In the course of the investigation and after some of our findings were reported, several papers appeared dealing with this subject, although of narrower scope, thus offering us the opportunity to compare our findings and conclusions.

## EXPERIMENTAL

### Polyamides

The polyamides investigated included both the regular and heat-stabilized varieties of nylon 66, poly(hexamethylene adipamide), and nylon 6, polycaprolactam, in the form of yarns and fabrics.

A total of six yarn specimens were used which had the following specifications.

Nylon 66, Type 300 (du Pont), was used in two different yarn constructions: 840 den., 140 filaments, 0.5 Z twists/in. (designated in the following as nylon 66 RA); 420 den., 68 filaments, 12 twists/in. (nylon 66 RB).

Nylon 66, Type 330 (du Pont), 420 den., 68 filaments, 12 twists/in. (nylon 66 HS), was a commercial yarn, stabilized to withstand exposure to elevated temperature. It is assumed that its essential difference from Type 300 yarn is its content of antioxidant.

Nylon 66 (donated by the Chemstrand Corporation), 840 den., 140 filaments, 0.5 twist/in., was an experimental yarn (nylon 66E) prepared from nylon 66 salt containing 0.06 mole-% of acetic acid as a molecular weight stabilizer.

Caprolan, 200 den., 32 filaments, 0.5 Z twist/in., was a polycaprolactam yarn donated by the National Aniline Division of Allied Chemical Corporation (nylon 6R).

Golden Caprolan, 840 den., 136 filaments, 0.5 Z twist/in., polycaprolactam yarn containing assumedly an antioxidant, was donated by National Aniline Division, Allied Chemical Corporation (nylon 6 HS). It had a yellow tint.

In our designations, R stands for regular commercial products, HS for heat-stabilized (i.e., containing an antioxidant) commercial products, and E for the experimental yarn.

All these fibers are bright, i.e., devoid of dulling pigments.

In reporting results, the numbers following the yarn designation give the exposure temperature (°C.) and time (minutes).

In most of the exposures, for easy handling, the yarn was knitted or woven into fabrics without addition of any lubricant or size. The breaking strength of the yarn was determined after mechanical separation of the warp and filling of the woven fabrics.

## Thermodegradative Process

### *Thermal Exposures Conducted in the Circulating Air Oven*

**Specimen Preparation.**  The yarn and fabric were mounted on rectangular metallic or wooden frames.  When yarn was used, it was wound manually in a single layer on the frame to permit free air circulation. Fabric specimens were supported in both the warp and filling direction by either sandwiching them between metallic frames or through the use of a wooden pin-frame.

The mounted specimens were subjected to a mild scouring treatment (20 min. wash in a 0.5% solution of a nonionic detergent (Triton X-100) at 50°C., followed by repeated rinsing in distilled water) prior to thermal exposure.  They were allowed to air dry and conditioned at 70°F. and 65% R.H. for at least 24 hr. before the exposure.

**Details of the Thermal Treatment.**  Thermal exposures were conducted in a circulating air oven which had a temperature control sensitivity of ±1.1°C. over the temperature range investigated (150–215°C.).

The mounted specimens were placed in a position perpendicular to the air stream in the oven at the derived temperature.  The oven temperature decreased somewhat but regained the test temperature in 1–2 min. as determined by iron–constantan thermocouple measurements.  The specimens were removed from the oven after predetermined time intervals, allowed to cool to room temperature, and conditioned for at least 24 hr. at 70°F. and 65% R.H.  The portion of the specimen in direct contact with and close to the frames was discarded and only the remainder used.

### *Thermal Exposures Conducted for the Rate Studies*

**Specimen Preparation.**  The nylon 66E knitted fabric was scoured for 20 min. in a 0.5% solution of a nonionic detergent (Triton X-100) at 70°C. followed by a repeated rinsing in distilled water.  The specimen was dried under vacuum (1 mm. Hg) at 70°C. for 3 hr., extracted continuously in a Soxhlet with ligroin for 4 hr., dried under vacuum (1 mm. Hg) at 70°C. for 4 hr., and stored in a desiccator over phosphorus pentoxide for at least 48 hr. before thermal exposure.

**Description of the Degradation Apparatus and the Heat Treatment.** The degradation chamber (Fig. 1) consisted of a three-necked, 2-liter flask in which the polyamide was suspended.  Heating was accomplished by immersing the flask in a heated oil bath regulated within ±0.5°C. of the required temperature.  Simultaneously, gas (air or nitrogen) preheated to the reaction temperature (±1°C.) was continuously fed into the degradation chamber at a rate of 2 l./min.  Gas temperatures were measured with an iron–constantan thermocouple.

When the exposures were conducted under nitrogen, the entire apparatus was first evacuated to 1 mm. Hg. pressure, the system purged with nitrogen for 10 min., and the process repeated two more times.  The nitrogen was freed from traces of oxygen by passing it through a train of alkaline pyro-
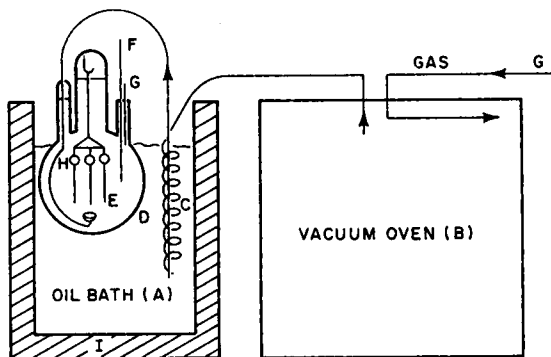
Fig. 1. Degradation apparatus: (A) oil bath with constant temperature regulation; (B) vacuum oven; (C) 10 ft. of ¹/₄ in. copper tubing, wound above the oil bath with electric heating tape, its temperature measured by surface pyrometer; (D) degradation chamber; (E) nylon specimens; (F) thermocouple; (G) gas outlet; (H) bulldog clips; (I) insulation.

gallol, Fieser's solution, concentrated sulfuric acid, phosphorus pentoxide, and a potassium hydroxide tower.

Approximately 50 g. portions of the purified and dried nylon 66E were heat-treated in either air or nitrogen for various time intervals at 136, 150, 168.5, and 192°C. Following exposure, the specimens were cooled by quickly raising the degradation chamber out of the oil bath and by passing gas maintained at room temperature, over the specimens for 25–30 min. The knitted fabric was unravelled, cut into short segments, hand carded to assure homogeneity, and stored individually in desiccators over Drierite.

## Physical and Chemical Evaluation of the Polyamides Before and After Thermal Exposure

### Tensile Properties

Breaking loads and breaking elongations of the yarns were determined from the endpoint of the stress–strain diagrams obtained from the Instron strain gauge instrument in the conditioning room after the specimens had been conditioned at 70°F. and 65% R.H. for at least 24 hr. The Instron was operated as follows: jaw speed, 2 in./min.; chart speed, 5 in./min.; full scale capacity, 10 or 20 lb.; specimen length, 5 in. (distance of jaws).

Twenty-five individual tensile tests were carried out on each specimen, and the following values were calculated: average breaking load and average breaking elongation variance, standard deviation, coefficient of variation, standard error of the mean, and standard error as per cent of the mean.

### Infrared Analysis

Yarn specimens were cut up into short segments, mixed with Dry Ice, and the mixture given two passes through a Wiley mill. The mixture was

then dried at 70°C. and 1 mm. Hg pressure over phosphorus pentoxide for 24 hr.

A 0.5–1.0% mixture of this finely ground polyamide sample in infrared grade potassium bromide was ground in a Wig-L-Bug for 60 sec. and the resulting mixture placed in a die and pressed at 100–125 psi for 3–5 min. under vacuum.

Infrared spectra were determined by using a Perkin-Elmer 221 infrared spectrophotometer.

### Electrical Resistivity

The electrical resistivities of the fabrics were measured with the aid of a megohmmeter having an upper limit of $10^{12}$ megohms. The measurements were conducted in an atmosphere of controlled relative humidity (usually 60%) with which the fabric had been equilibrated for at least 24 hr. beforehand.

Since nylon fabric has a high specific and surface resistivity, it was necessary to use large electrodes through a short distance. In the first series of measurements, bulldog clips were used as electrodes which were hung on wire supported by Teflon blocks. In later experiments, the fabric was laid flat on a brass plate resting on a polyethylene block. This plate served as one of the electrodes. The second electrode was a brass plate of identical dimension placed on the top of the fabric.

### Moisture Absorption

Moisture regain determinations on yarn and fabric specimens were carried out in accordance with Method 2600 of Federal Specification CCC-T-191b (oven and desiccator method).

### Acid Sorption of Nylon 66

Yarn specimens were cut into 1-in. lengths, hand carded to assure homogeneity, and conditioned at 70°F. and 65% R.H. for at least 24 hr. prior to the acid sorption experiments. The rate and equilibrium acid-binding capacities of the polyamides were determined as follows.

Into a 250-ml. single-necked flask containing the conditioned polymer (10.00 g. on a bone-dry basis) were pipetted 100 ml. of hydrochloric acid (pH = 2.23) which had previously been conditioned in an oil bath maintained at 60% ±1°C. The flask was attached to a condenser and immersed in the oil bath at 60°C.

At a predetermined time, approximately 50 ml. acid solution was pipetted into a 150 ml. beaker and weighed. The beaker, covered with aluminum foil, was cooled to room temperature and the acid titrated potentiometrically with 0.02$N$ sodium hydroxide. The instrument used was a Beckman Model G pH meter. Suitable blank determinations were also run.

## Endgroup Analysis

**Amine Endgroup Content.** The total number of amine groups present in the polyamides was determined by the procedure reported by Waltz and Taylor[2] by conductometric titration of the phenolic solution.

**Carboxyl Endgroup Content.** Carboxyl contents of unexposed or non-discolored polyamides were determined by a modified Waltz-Taylor method[2] which involved titration of a hot benzyl alcohol solution under nitrogen, $0.1N$ alcoholic potassium hydroxide being used as the titrant and phenolphthalein as the indicator.

The indicator technique did not prove suitable for specimens which were appreciably discolored due to heat treatment in air. An apparatus was therefore devised which allowed us to titrate conductometrically. The polymer solution in benzyl alcohol was maintained at 180°C. with the aid of an ethylene glycol vapor bath.

## Viscosity-Average Molecular Weights

The procedure used for determining viscosity-average molecular weights was that reported by Mele and Liquori,[3] who determined the values of the Staudinger constants $K$ and $a$ for nylon 66 in 85% formic acid at 25°C.

The solvent, 85.0% formic acid, was prepared by appropriately diluting 88% formic acid (Fisher Certified Reagent) with distilled water. The solvent concentration was confirmed by titration.

## RESULTS AND DISCUSSION

### Tensile Strength

The tensile strength of the yarn was measured as a technical indication of polymer degradation and in order to limit the investigation to a range of conditions in which the properties approach or reach the lower limit of technical usefulness. Arbitrarily, the maximum severity of exposure was selected to correspond to a reduction of the breaking strength to 40–50% of the original value. The strength and breaking elongation of the un-treated samples measured under standard conditions are listed on Table I. As we see, the regular and the heat-resistant nylon 66 yarn had the same

TABLE I
Breaking Strength and Elongation of Untreated Yarns

| Yarn | Breaking strength, lb. | Denier | Breaking elongation, % |
|---|---|---|---|
| Nylon 66RA | 14.0 | 840 | 17 |
| Nylon 66RB | 7.0 | 420 | 17 |
| Nylon 6R | 2.1 | 200 | 19 |
| Nylon 66HS | 7.0 | 420 | 17 |
| Nylon 6HS | 14.0 | 840 | 17 |

mechanical properties. The regular nylon 6 sample was much weaker, but the heat-resistant nylon 6 was as strong as the nylon 66 yarn. Obviously, the heat-resistant nylon 6 differed from the regular one not merely by the presence of a stabilizing additive.

On exposure to elevated temperature in the presence of air, nylon 66 lost its strength, depending on the severity of the exposure, as seen in Figure 2. In crude approximation, in the sensitive range of 176–221°C. an increase of 10°C. of the temperature was equivalent to a 50% extension of the exposure time.
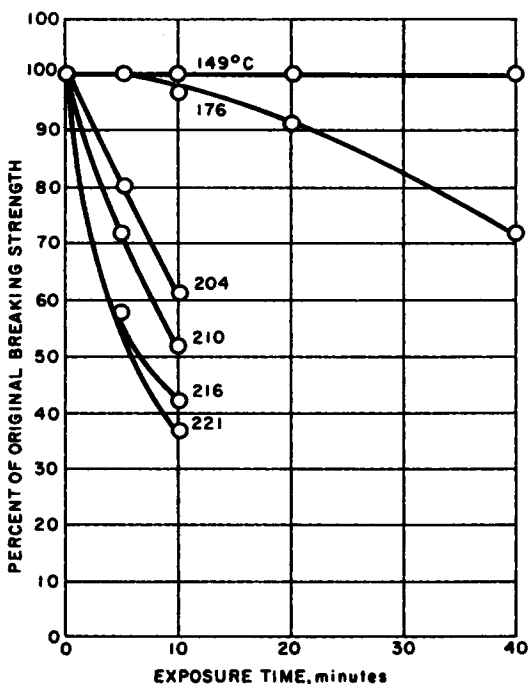


Fig. 2. Effect of time and temperature of exposure in air on the breaking strength of nylon 66 yarn.

Nylon 6R was similarly affected by the exposure to air.

The loss of breaking strength was in every case accompanied by a proportional loss of the breaking elongation; i.e., the secant modulus to break was practically unchanged.

The stabilized yarns, nylon 66HS and nylon 6HS proved, as expected, much more resistant to hot air. For all practical purposes their mechanical properties remained unchanged during exposure for 10 min. up to 216°C.

However, on prolonged exposure, even the heat-stabilized nylons lose their strength. As Nesty[4] reported, these nylons lose about 60% of their strength at 176°C. in 100 hr. and at 220°C. in a few hours.

In order to assess the role of air in the heat degradation process, samples of nylon 66R and nylon 6R were exposed to 168°C. for 90 min. in air and also in a stream of preheated, oxygen-free nitrogen under otherwise identical conditions.   In air the breaking strength was reduced to 9.35 lb. (33% loss), in nitrogen to 13.8 lb. (2% loss).   These and a series of similar experiments proved conclusively that the degradation in air is essentially oxidative in nature and the heat resistant yarns behave as if protected by antioxidants.

## Effects of Exposure on Moisture Regain

Exposure to heat invariably reduced the equilibrium moisture content of the yarn measured under the standard condition of 65% R.H. and 70°F., independent of the presence or absence of oxygen or antioxidant in the fiber.   The original value was 3.4–3.7%; on exposure the value appeared to approach approximately 2.4% (Table II.)

Munden[5] noted that treatment of nylon 66 at temperatures of about 200°C. increases x-ray crystallinity and at the same time decreases the moisture regain considerably.   Since our findings were reported, Peters and White[6] published the results of experiments showing the reduction of the moisture regain from 4.02% to 2.98% as a result of exposure of nylon 66 yarn for 5 min. to a temperature of 200°C. in air.   These observations are in close agreement with ours.

The effect might be explained by secondary crystallization in a broad sense of the word.   If we assume that the crystalline region does not absorb any water and that the amorphous region absorbs a constant amount (certainly an oversimplification), the observation indicates that exposure to heat can reduce the amount of amorphous polymer present by as much as 40% of its original value.   Assuming, with Valentine,[7] that at 65% R.H. each amide group combines with 0.57 molecules of water, nylon should absorb, if completely amorphous, 9% water.   A 4% moisture regain would correspond to a polymer consisting of 44% amorphous and 56% crystalline material.   Our heat-treated nylon of 2.4% moisture regain should then contain 27% amorphous and 73% crystalline material.

TABLE II
Effect of 10-Min. Exposure in Air at Various Temperatures
on the Moisture Regain of Nylon Yarns

| Exposure temperature, °C. | Average moisture regain, % | | | |
|---|---|---|---|---|
| | Nylon 66 | Nylon 66HS | Nylon 6 | Nylon 6 HS |
| Control | 3.73 | 3.65 | 3.48 | 3.39 |
| 149 | 3.26 | 3.26 | 3.10 | 3.11 |
| 176 | 3.11 | 3.07 | 2.95 | 2.88 |
| 190 | 3.02 | 2.75 | 2.93 | 2.69 |
| 204 | 2.56 | 2.51 | 2.54 | 2.57 |
| 216 | 2.49 | 2.51 | 2.49 | 2.50 |

## Effect of Thermal Exposure on Electrical Resistivity

As expected from the observation of the moisture, absorption exposure to dry heat considerably increased the resistivity of the polyamide. For example, if the unexposed fabric showed a resistivity in the low $10^{10}$ ohm range, an exposure to 200°C. for 10 min. sufficed to bring it to the middle $10^{11}$ ohm range.

## Effect on the Absorption of HCl

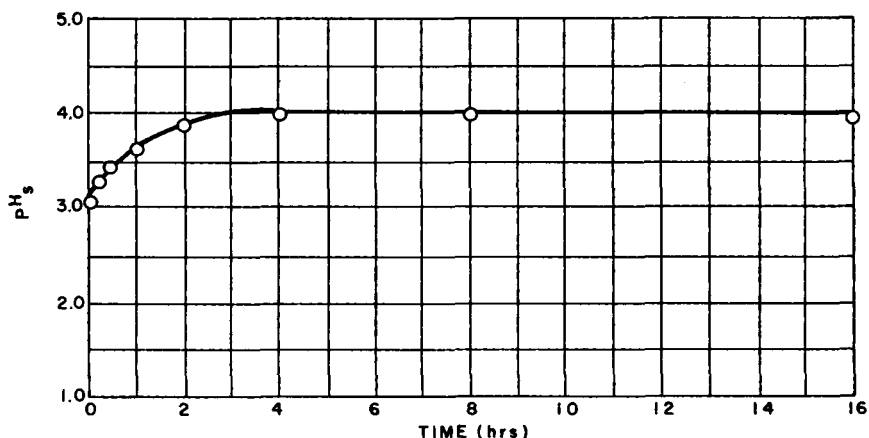The equilibrium acid-binding capacity of a polyamide is a measure of the number of accessible amine groups.



Fig. 3. Change of pH of HCl solution upon the immersion of untreated nylon 66 yarn.

Although it was often reported that the take-up of dyes, and specifically, of anionic dyes by nylon is reduced by heat treatments such as heat setting, no data are available on the effect on the take-up of simple acids.

Figure 3 shows the gradual absorption of the acid manifested by the increase of the pH of the acid solution ($pH_s$) in contact with untreated nylon with time at 60°C.

Figure 4 shows the amount of bound acid as a function of the square root of time expressed as equivalents/kilogram of fiber at an initial pH of 3.04 and final pH of 3.97 of the bath.

The results indicate that in 2–4 hr. an apparent equilibrium is reached, within the limits of experimental error.

The acid binding capacity of nylon 66R at 60°C. was determined at several pH values in the range 2–4 after immersion for 16–29 hr. This seemed more than sufficient to establish equilibrium. The data are plotted in Figures 5 and 6.

The rate curves have the characteristics of a diffusion process. The take-up is linear with the square root of the time until approximately two-thirds of the equilibrium sorption is reached. We deal here with diffusion
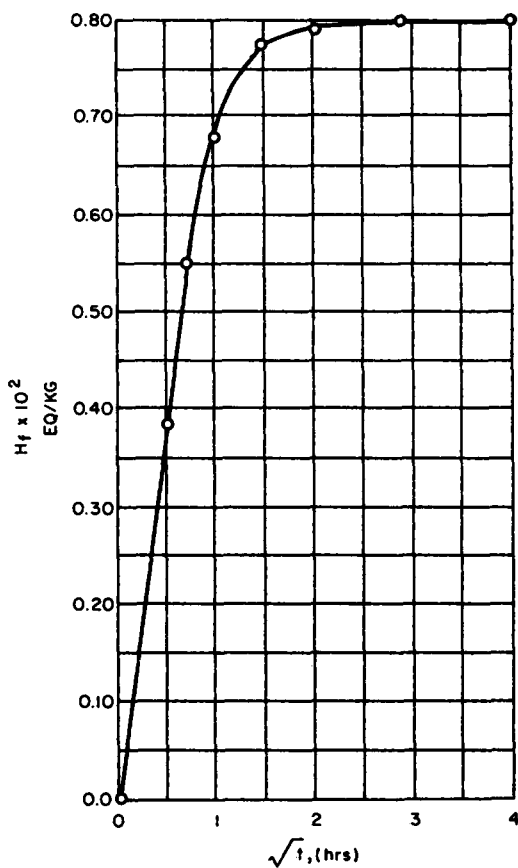
Fig. 4. Rate of sorption of HCl (initial pH = 3.04) by untreated nylon 66 yarn (in mole HCl/kg. nylon).
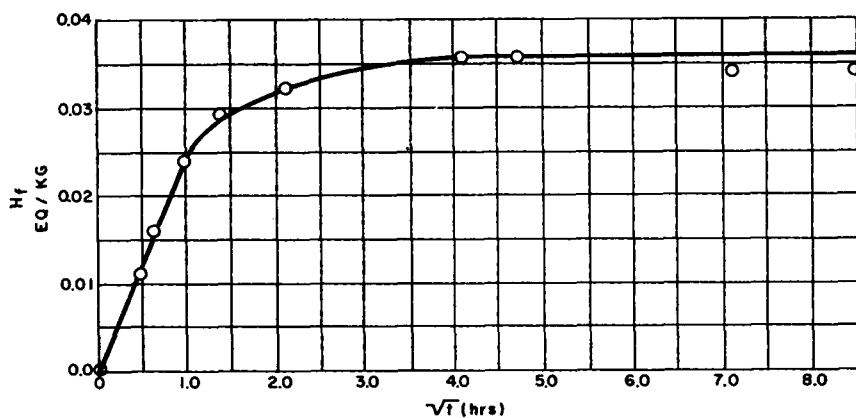


Fig. 5. Rate of sorption of HCl (initial pH = 2.20) by untreated nylon 66 yarn (in mole HCl/kg. nylon).

from a finite bath into an infinite cylinder.    The data would allow us to calculate the value of an apparent diffusion coefficient, taking into account the effect of adsorption, e.g., in following Crank's[8] theory.    We notice that the time required to reach an absorption equal to half of the equilibrium
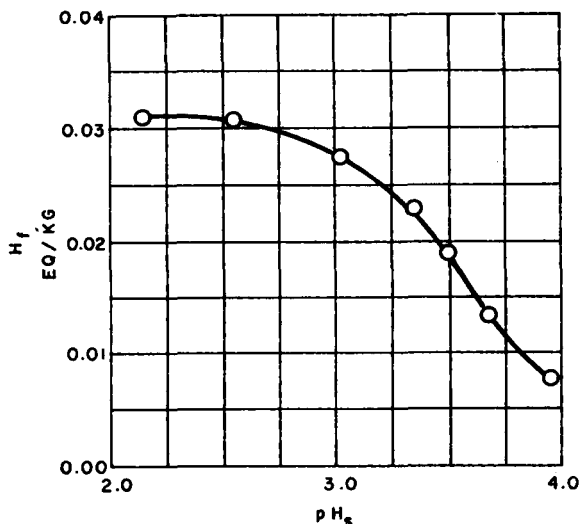


Fig. 6. Apparent equilibrium sorption of HCl (mole HCl/kg. nylon) by untreated nylon 66 yarn as a function of the final pH.
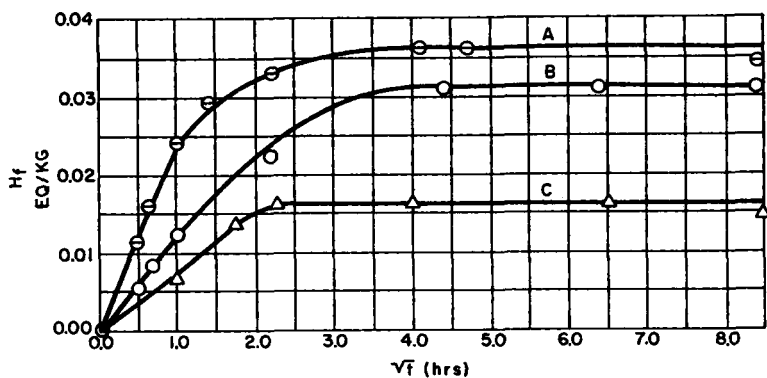


Fig. 7. Rate of sorption of HCl (initial pH = 2.20) (in mole HCl/kg. nylon):    (A) untreated nylon 66; (B) nylon 66 exposed to air for 10 min. at 176°C.; (C) nylon 66 yarn exposed to air for 10 min. at 216°C.

value is somewhat less at the higher pH value (approximately 0.27 hr.) than at the lower pH value (approximately 0.51 hr.).    At equilibrium, only 25% of the saturation value is absorbed in the first case, but more than 90% on the second case.    The theory would demand for a constant apparent diffusion coefficient a considerable reduction of the time required
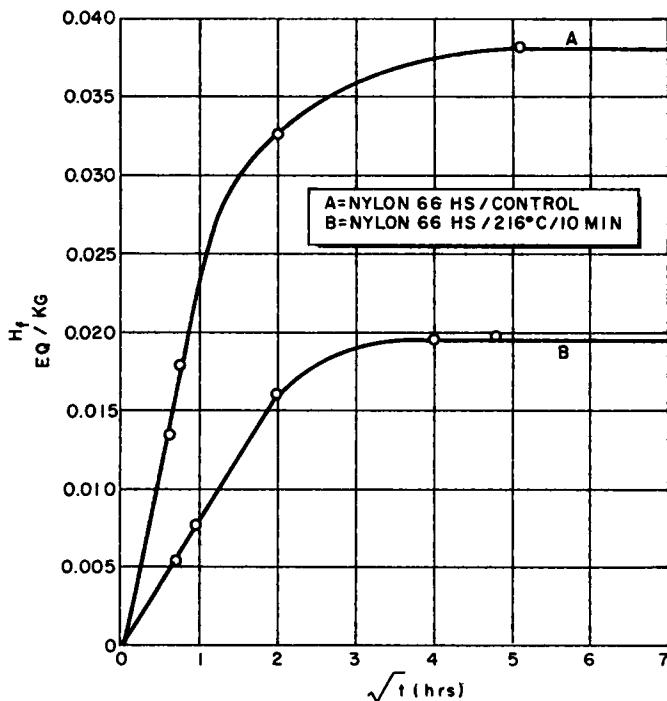
Fig. 8. Rate of sorption of HCl (in mole HCl/kg. nylon) at an initial pH of 2.20: (A) untreated, heat-stabilized nylon 66; (B) heat-stabilized nylon exposed in air to 216°C. for 10 min.

for a given level of absorption (relative to the equilibrium value) with increasing equilibrium value, i.e., the opposite behavior observed by us.

A possible explanation for this anomaly is the increase in the Donnan potential caused by the increased hydronium absorption at the lower pH level. In this respect, our system is radically different from the one used for the study of the rate of dyeing with acid dyes, where the pH is maintained constant and only the dye concentration is varied. There are indications in the literature[8] that the Donnan potential (or surface potential) is an important factor in reducing the rate of absorption of ions.

The data allow us to make the following conclusions.

(1) The process of acid binding does not continue indefinitely and is essentially terminated in a few hours at 60°C.

(2) Under these experimental conditions irreversible hydrolytic effects can be disregarded. This effect, if significant, would have caused a steady increase in the amount of acid bound with increasing time.

(3) The acid-binding capacity of nylon 66 at 60°C. is $0.035_5$ equiv./kg. of dry nylon when the acid solution has a final pH of 2.55, and this represents probably a saturation of the accessible amine groups.

Our findings should be compared with the values of Lemin, as published by Vickerstaff.[9] These were determined at room temperature after a one

week immersion.   Although Lemin's values likewise show a flattening off
in the pH range 2.5–2.7, this is less pronounced than in our case.   Lemin's
value for acid-binding capacity at pH 2.55 is practically the same as ours.

After a reference standard had been established for untreated nylon 66,
specimens which were exposed at 176 and 216°C. for 10 min. in air were in-
vestigated.

A comparison of the acid-binding behavior of untreated and heat-exposed
nylon is presented in Figure 7.   Curve $A$ represents the amount of acid
bound by the untreated nylon; curves $B$ and $C$ refer to the acid-binding
characteristics of the nylon specimens exposed at 176 and 216°C., re-
spectively.

It can be seen that the severity of the thermal treatment influences the
degree to which the acid sorption is retarded.   If the time necessary to
reach a sorption equal to half of the equilibrium value can be regarded as
a measure of the rate of sorption, our observation tends to indicate a "tight-
ening" of the polymer structure as induced thermally, and is in accordance
with the findings of moisture regain and electrical resistivity measurements.
This tightening might result in a higher degree of tortuosity of the path of
the hydronium ion (accompanied by the chloride ion) or in a lowered
mobility of the polyamide segments of the "amorphous" phase.   The
latter possibility is also indicated by the higher initial modulus of the heat-
treated samples.   It is not surprising that numerous investigations[10,11]
reported the decrease of the rate of dyeing with acid dyes after heat ex-
posure of nylon.

The acid-binding capacity of the nylon at equilibrium also decreased
from $0.35_5$ equiv./kg. for the untreated nylon to $0.032_0$ and 0.015 equiv./kg.
for the specimens treated at 176°C. and 216°C., respectively.   Obviously,
the end pH was lower with the exposed samples, so that the differences
could be even greater if they could be related to identical end pH values.

The acid-binding behavior of nylon 66HS before and after thermal ex-
posure to 216°C. in air for 10 min. was also investigated (Fig. 8).

Inspection of Figures 7 and 8 reveals that the retardation in rate of acid
sorption and the decrease in acid-binding capacity at equilibrium caused
by the thermal treatment is essentially the same for both stabilized and
nonstabilized nylon 66.

The question as to whether some of the amine endgroups became in-
accessible or were actually eliminated as a consequence of the heat treat-
ment was pursued by investigating the polyamides in the dissolved state,
as reported below.

### Effect on Amine and Carboxyl Group Content

The determination of titratable amine groups of the dissolved nylon
showed that thermal exposure in air eliminates such groups, regardless of
the presence of antioxidants.   (Table III, third column.)

On comparing these data with those of HCl absorption, it can be seen
that only 80% of the amine groups in the unexposed nylon and only 55%

TABLE III
Analytical Results on Nylon 66R and Nylon 66HS before and
after Thermal Exposure in Air

| Yarn | Exposure | Amine content, equiv./kg. | Carboxyl content, equiv./kg. | Viscosity-average molecular weight $\bar{M}_v$ |
|------|----------|---------------------------|------------------------------|-----------------------------------------------|
| Nylon 66R | Control | 0.045 | 0.086 | 13,340 |
| Nylon 66R | 176°C./10 min. | 0.040 | 0.082 | 13,490 |
| Nylon 66R | 216°C./10 min. | 0.028 | 0.082 | 8,892 |
| Nylon 66HS | Control | 0.046 | 0.083 | 12,940 |
| Nylon 66HS | 216°C./10 min. | 0.029 | 0.082 | 16,180 |

in the heat-exposed (216°C./10 min.) nylon participates in the combination with acid at pH 2.5. Apparently, a significant portion of these amino groups is inaccessible in the fiber, and the heat treatment not only eliminates some of the amino groups, but also reduces the accessibility of the remaining groups. This can be due to the secondary crystallization as indicated by the reduction of the moisture absorption or to the preferential elimination of the originally accessible groups.

The rate of amino group elimination was followed in greater detail on the experimental nylon 66 sample and is shown in Figure 9.
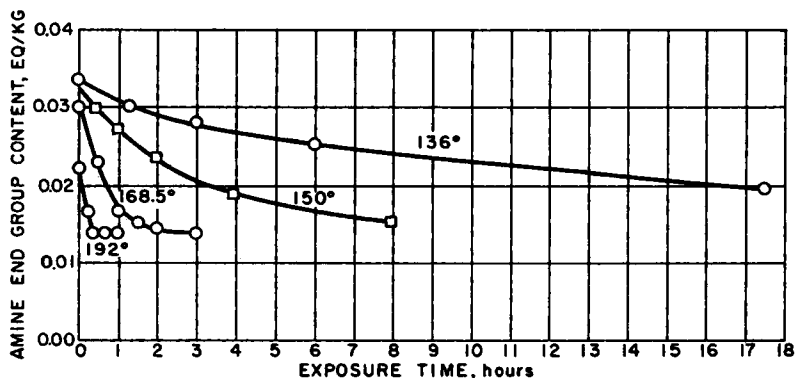


Fig. 9. Effect of exposure to air at various temperatures on the amine content of nylon 66E.

On exposure in nitrogen, the amino group content decreased only slightly; the loss amounted to only 10% on exposure for 1 hr. to 192°C.

Zollinger[12] noted recently that dry heat decreased the number of amino groups in nylon.

Since our findings were reported,[1] Peters and White[6] published the results of experiments showing the reduction of amino endgroup content from approximately 0.043 to 0.032 meq./kg. as a consequence of exposure of

nylon 66 yarn for 1 min. to 215°C. in air.    These figures are within the broad limits of possible comparison in agreement with ours.

Whether the loss of amino groups is related to the weight loss of the nylon reported to occur on prolonged heat exposure appears dubious. Nesty[4] reported a loss during exposure in air at 185°C. for one day to amount to 2.2% for heat-stabilized nylon 66 and to 5.7% for unstabilized nylon 66.    In nitrogen, under the same conditions, the losses amounted to 1.3 and 2.5%, respectively.    We found the loss of amino groups in air less affected by the presence or absence of antioxidant, but sensitive to the presence or absence of air.

The exothermic reaction initiating in air around 185°C., but absent in nitrogen, observed by Schwenker[13] on differential thermal analysis of nylon, is probably related to the reaction causing loss of the amino endgroup.

The determination of the carboxyl groups was less precise than that of the amines, but the data of the fourth column of Table III shows that not more than 5% was lost at the most severe exposure.

### Effect on the Viscosity-Average Molecular Weights

The viscosity-average molecular weights of the nylon 66R and nylon 66HS specimens before and after thermal exposure for 10 min. in air at 176°C. and 216°C. are listed in the last column of Table III.

The viscosity-average molecular weights were also determined for the nylon 66E specimens which were thermally exposed in air and nitrogen for various time intervals at 136, 150, 168.5, and 192°C., these are recorded in Figure 10.
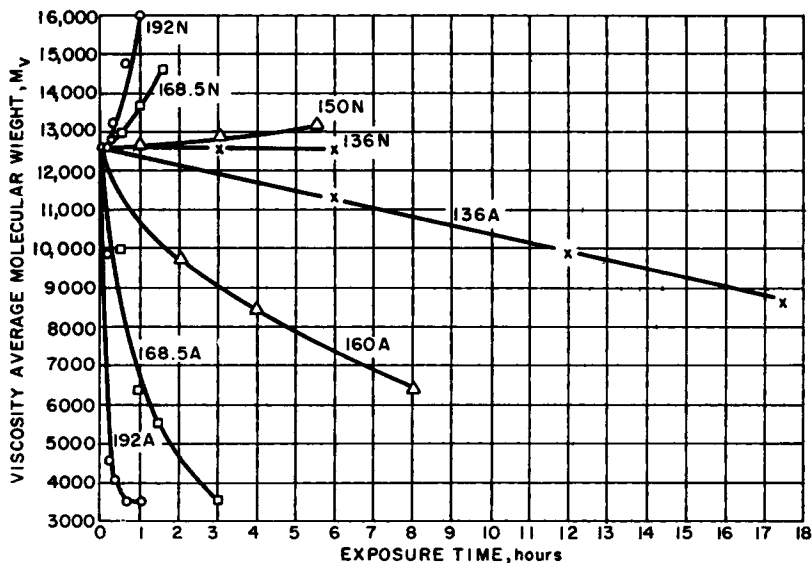


Fig. 10.    Effect of exposure to various temperatures in air (A) and in nitrogen (N) on the viscosity-average molecular weight of nylon 66E.

## Interpretation of Molecular Weight Changes

The data show that the molecular weight of nylon 66 decreases on heating in presence of air but increases on heating in presence of antioxidants or in presence of nitrogen. Obviously, the action of oxygen causes cleavage, but heat alone causes the polymeric molecule to crosslink. It is reasonable to assume that in oxygen probably some crosslinking also takes place, but its effect is overshadowed by the simultaneous scission.

Comparison of the viscosity-average molecular weight with number-average molecular weight calculated merely from the carboxyl and amino endgroup content shows the latter values to be consistently higher. It follows that other endgroups must be present. In case of the experimental sample, nylon 66E, the number of acetyl groups is known. However, even in this case, the amine and acetyl groups add up to only $36 \times 10^{-6}$ equiv./g., i.e., to an endgroup molecular weight of 28,000 against the viscosity-average molecular weight of 12,600. Interestingly, the number of carboxyl groups is twice as large ($74 \times 10^{-6}$ equiv./g.) and, assuming that each molecule terminates at one end in a carboxyl group, the molecular weight would calculate to 13,500. At least one-fourth of the endgroups must be still other than amine, acetyl, or carboxyl.

As the oxidative cleavage progresses, the viscosity-average molecular weight drops. At the same time, the number of amine groups drops and the number of carboxyl groups remains about constant. It is, therefore, obvious that the cleavage creates endgroups of unknown nature, other than amine or carboxyl.

These observations are possibly related to those made by Weltzien et al.,[14] who reported that the amino endgroup number-average molecular weight of a nylon 6 fiber (Perlon) is, in general, higher than the viscosity-average molecular weight. Before spinning into fiber, the polyamide exhibits approximately the same viscosity-average molecular weight as after spinning. The amino endgroup number-average molecular weight is, however, much lower before than after spinning; it is about equal to the viscosity-average molecular weight. In other words, during spinning, the number of amino groups decreases, whereas the solution viscosity remains unchanged. The carboxyl endgroup content was virtually unaffected by spinning.

In our experiments with nylon 66R and nylon 66HS, the effect of exposure to 216°C. for 10 min. in air seemed to be similar in some respects to the changes observed by Weltzien and co-workers, i.e., a decrease of the amino groups without a corresponding decrease of the carboxyl groups. It should be borne in mind, however, that the spinning process is conducted at higher temperatures and in the absence of oxygen. When our exposures were repeated under nitrogen, the reductions in amine endgroup content were found almost negligible.

The crosslinking reaction, which occurs with heat-stabilized nylon in air and with regular nylon in nitrogen appears not to be based on continuing

polycondensation, as the carboxyl group content fails to exhibit sufficient drop.

Harding and MacNulty[15] investigated the effect of heat exposure in air on molded nylon specimens and noted that the viscosity-average molecular weight of the surface layer decreased, but that of the bulk increased. They concluded that the oxidation reaction prevails on the surface, but a condensation reaction takes place simultaneously in the interior. After 6 hr. at 200°C. and after 0.5 hr. at 250°C. an increasing portion of the surface layer becomes insoluble. Interestingly, the material from the interior remains completely soluble. This observation would indicate that the condensation, in absence of oxygen, occurs at the ends of the polymer chain rather than along the chain. In contrast to this, Rafikov and Sorokina[16] emphasize the formation of branched and of three-dimensional structures on thermo-oxidative aging. Their data, however, show insolubilization after 8 hr. exposure only at their highest experimental temperature, namely at 200–205°C. Kamerbeek et al.[17] observed that in nitrogen at 305°C. it took more than 5 hr. before the nylon became incompletely soluble. These observations agree with our own finding that under the exposure conditions of our experiments no insolubilization occurred.

There are several observations in the literature (Sharkey and Mochel,[18] Cannepin and Baulenas,[19] Nolin[20]) indicating that the attack of oxygen on amides occurs at the methylene group adjacent to the nitrogen and leads to the formation of aldehydes. Kamerbeek et al.[17] investigated the photo-oxidation of nylon by identifying the degradation products and concluded that they originate from the cleavage of the bond between amide nitrogen and the adjacent methylene. For the reaction leading to increased molecular weight Hill,[21] Meacock,[22] and Kamerbeek and co-workers[17] suggested the formation of secondary amines by condensation of amine endgroups under elimination of ammonia.

## Activation Energy of the Oxidative Processes

The rate constants for the elimination of the amine groups of nylon 66 in air at three temperatures were determined on basis of the data recorded in Figure 10. It was assumed that the concentration of oxygen was constant due to the high velocity of air flow around the exposed yarn. The implication of this assumption will be discussed below.

The curves indicate that with progressive exposure the amine content approaches a limiting value of 0.0141 equiv./kg. Assuming that this portion of the amine group is inaccessible to oxygen, possibly due to its location in the crystalline portion, we calculate the amount of originally accessible amine groups to be 0.019 equiv./kg. Plotting the ratio of originally accessible groups to the remaining accessible groups logarithmically against the exposure time, we obtained straight lines (Fig. 11). This allows, by application of first-order kinetics, calculation of the rate constants (Table IV). The constants follow the Arrhenius equation, i.e., their logarithms give a straight line against the reciprocal values of the absolute tempera-
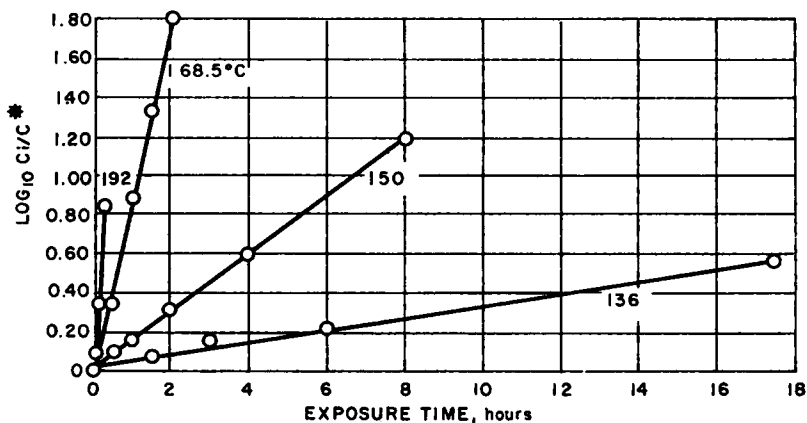
Fig. 11. Rate of elimination of amine groups from nylon 66E on exposure to air at various temperatures, expressed as logarithm of the ratio of accessible amine groups originally present ($c_1$ = 0.019 equiv./kg. nylon) to accessible amine groups present at time $t$ ( = $c^*$).
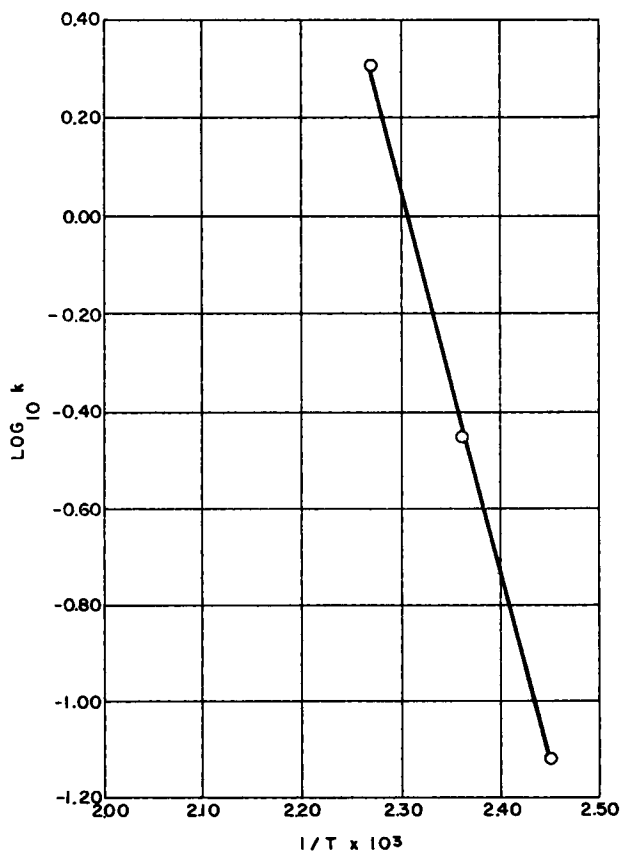


Fig. 12. Arrhenius plot for the elimination of amine groups from nylon 66E on exposure to air.
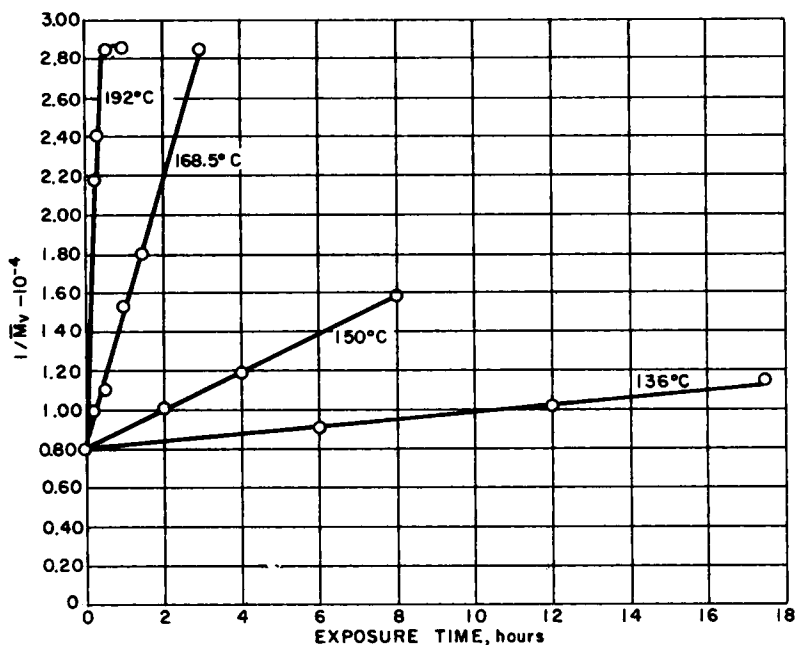
Fig. 13. Rate of cleavage of nylon 66E on exposure to air at various temperatures expressed as the reciprocal value of the viscosity-average molecular weight.

ture.    The slope (Fig. 12) corresponds to an activation energy of 36 kcal./mole.

TABLE IV
Rate Constants for the Reaction(s) Leading to the Disappearance of
Amine Groups upon Heat Treatment of Nylon 66 in Air

| Temperature $T$, °K. | $1/T \times 10^3$ | Apparent rate constant $k$, hr.$^{-1}$ | $\log k$ |
|---|---|---|---|
| 409 | 2.45 | 0.0755 | 1.1211 |
| 423 | 2.36 | 0.346 | 0.4609 |
| 441.5 | 2.27 | 2.04 | 0.3096 |

TABLE V
Overall Rate Constants for the Cleavage upon Heating
Nylon 66E in Air

| Temperature $T$, °K. | $1/T \times 10^3$ | Overall rate constant $k$, mole/g.-hr. |
|---|---|---|
| 409 | 2.45 | $1.72 \times 10^{-6}$ |
| 423 | 2.36 | $9.75 \times 10^{-6}$ |
| 441.5 | 2.27 | $6.88 \times 10^{-5}$ |

In order to calculate the rate constant for the cleavage of the nylon 66 molecule on exposure in air, the reciprocal values of the viscosity-average molecular weight were plotted against the time.    The plots formed straight
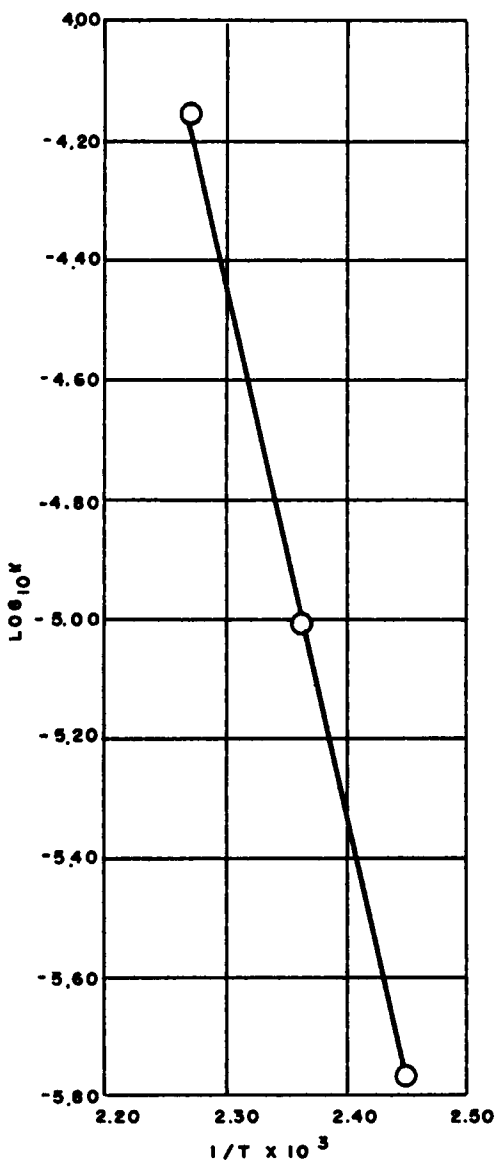


Fig. 14.    Arrhenius plot for the cleavage of nylon 66E on exposure to air.

lines at the lower three temperatures (Fig. 13).    This allowed also the application of first-order kinetics (Table V).    An Arrhenius plot was obtained corresponding to an energy of activation of 40 kcal./mole (Fig. 14).

## Role of Diffusion of Oxygen in the Fiber

The ultimate justification for the assumption that the oxygen concentration in the fiber can be regarded constant could only be supplied if the rate of the reaction would be found independent of the specific surface, i.e., of the fineness of the filament. We have not carried out such an investigation, but assumed that the diffusion rate of such a small molecule as oxygen in the amorphous phase of the polymer at temperatures high above the glass transition temperature will be not much less than of the order of the diffusion rate of gases in liquid ($D \sim 10^{-5}$ cm.$^2$/sec.). In this case, the rate of penetration of the gas would be by several orders of magnitude faster than its disappearance. From the behavior of small organic molecules, it also appears unlikely that the disappearance of amino groups and the scission of secondary amides should proceed instantaneously at temperatures between 136 and 215°C. in case of free availability of oxygen. Simultaneously with the presentation of this paper, however, Zimmerman et al.[23] presented a paper which appears to suggest that oxygen diffusion is controlling the thermal degradation of polyamide fibers and films. They point out that the irreversible reaction of the oxygen could slow down its progress in the polymer. In this connection, it is noteworthy that observations by Harding and MacNulty[16] indicated that the oxidative degradation in a molded specimen of nylon 66 at 150°C. penetrated in 166 hr. to a depth somewhere between 120 and 240 $\mu$. Assuming the rate of penetration to be proportional to the square root of time, it would take approximately 1 hr. for the oxygen to reach the center of the cross section of a cylinder of the dimension of the fiber. On exposure of the fiber for 1 hr. at 153°C., we find that some 23% of the amine endgroups were eliminated. It is, however, not known how the rate of diffusion in the radial direction of the oriented fiber relates to the rate in the molded piece. Therefore, the possibility cannot be disregarded that the activation energy of the diffusion at least contributes to the overall activation energies observed.

This paper was taken from the dissertation submitted by one of the authors (C. K. C.) to the Faculty of Lowell Technological Institute in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

*Note added in proof:* After completion of the manuscript a series of papers on the effects of steam and heat setting on nylon 6 fibers was published by Koshimo and co-workers [*J. Appl. Polymer Sci.,* **9,** 1–139 (1965)]. The reduction of the moisture absorption on dry heat setting reported by Koshimo and Tagawa [*J. Appl. Polymer Sci.,* **9,** 45 (1965)] is in agreement with our observations. These authors consider a closer packing in the amorphous region as the main cause of the change.

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## Résumé

Des fils de nylon 66 et de nylon 6 ont été soumis a l'air sous atmosphère d'azote et sous vide à des températures allant de 136 à 215°C pendant des périodes allant de 5 min. à 17,5 heures. L'absorption d'humidité de ces deux fibres a été réduite par l'exposition à ces conditions, indépendamment de la présence d'oxygène ou d'antioxydant. Cela est

attribué à la cristallisation secondaire. Simultanément, la résistivité électrique est augmentée. La force de rupture est réduite par exposition en présence d'oxygène sauf si le polymère contient un antioxydant. L'étendue de la rupture oxydante a été mesurée au moyen du poids moléculaire moyen viscosimétrique ($\bar{M}_v$) du nylon 66. Simultané-ment on observe une diminution de la teneur en groupement amine terminal. Cela a lieu uniquement en présence d'oxygène et tend vers une limite, ce qui indique que cer-tains groupes aminés ne subissent pas l'élimination. S'il n'y a pas d'oxygène ou si le polymère est protégé par un antioxydant, $\bar{M}_v$ augmente. La sorption d'acide chlor-hydrique est réduite par l'exposition. Seulement 80% des groupements amines dans le nylon non-exposé et 55% dans le nylon exposé participent a fixation d'acide à pH 2,5. Les constantes de vitesse de la rupture, manifestée par $\bar{M}_v$, et du processus conduisant à la disparition des groupements aminés, ont été déterminés pour le nylon 66. Les énergies d'activation calculées sont de 40 et 36 Kcal/moles respectivement.

## Zusammenfassung

Nylon-66- und Nylon-6-Garne werden unter Luft, Stickstoff und im Vakuum für Perioden von 5 min bis 17,5 h von bei Temperaturen 136 bis 215°C gehalten. Die Feuchtigkeitsabsorption beider Fasern wird durch diese Behandlung unabhängig von der Gegenwart von Sauerstoff oder eines Antioxydans herabgesetzt. Dies wird auf sekundäre Kristallisation zurückgeführt. Gleichzeitig steigt der elektrische Widerstand an. Die Bruchfestigkeit wird durch Behandlung in Gegenwart von Sauerstoff, ausser bei Gehalt des Polymeren an einem Antioxydans, herabgesetzt. Das Ausmass der oxy-dativen Spaltung wurde durch den Viskositätsmittelwert des Molekulargewichts ($\bar{M}_v$) von Nylon-66 gemessen. Gleichzeitig wurde eine Verringerung des Aminoendgruppenge-haltes beobachtet. Diese findet nur in Gegenwart von Sauerstoff statt und nähert sich einem Grenzwert, was zeigt, dass einige Aminogruppen keiner Eliminierung unterliegen. Bei Abwesenheit von Sauerstoff oder Schutz des Polymeren durch ein Antioxydans nimmt $\bar{M}_v$ zu. Die Sorption von Chlorwasserstoffsäure wird durch die Behandlung herabgesetzt. Nur 80% der Aminogruppen im unbehandelten und 55% im behandelten Nylon nehmen bei pH 2,5 an der Säurebindung teil. Die Geschwindigkeitskonstanten der durch $\bar{M}_v$ gemessenen Spaltung und des zum Verschwinden von Aminogruppen führenden Prozesses wurden für Nylon-66 bestimmt. Die Aktivierungsenergie wurde zu 40 bzw. 36 kcal/mol berechnet.