Determination of Hydroperoxides in Ultraviolet-Irradiated Nylon 66

ANTHONY ANTON, *Carothers Research Laboratory, Textile Fibers Department, E. I. du ·Pont de Nemours and Company, Inc., Wilmington, Delaware*

Synopsis

According to mechanisms described in the literature, photodecomposition of nylon 66 proceeds through the abstraction of the hydrogen on the carbon α to the amide NH group by a free radical which has been activated by photo absorption. In the propagation phase, the α-carbon radical could readily react with atmospheric oxygen to form a hydroperoxide. The formation of a hydroperoxide in the photodecomposition scheme for nylon 66 has been detected but has not been measured quantitatively. With the colorimetric method described in this paper, it is now possible to determine the peroxide content in a polyamide to a level of 1 μmole/g. with a relative precision of less than 5%. The polyamide is dissolved in tetrafluoropropanol, to which aliquots of potassium iodide and glacial acetic solutions are added. The absorbance of the liberated iodine is measured in a 1-cm. cell at 400 mμ and the hydroperoxide concentration determined from a calibration curve constructed from hydrogen peroxide solution standards. The rate of peroxide formation, which is dependent on the wavelength of ultraviolet radiation, can be correlated to the strength loss exhibited by a nylon 66 yarn free from antioxidant and delustrant. In addition, an increase in the level of thermal degradation will accelerate yarn strength loss and peroxide formation under ultraviolet exposure. The hydroperoxide begins to decompose at about 100°C. Yarn finish will contribute to the peroxide formation during exposure.

INTRODUCTION

The photodegradation of nylon 66 has been studied by a number of investigators.[1–4] According to these publications, the degradation reaction is initiated by a free radical, produced by photon absorption at a proper wavelength, which proceeds to abstract the hydrogen on the carbon α to the amide NH. The new radical formed on the polyamide chain can react with atmospheric oxygen to form hydroperoxides. These hydroperoxides can decompose especially under heat to form aldehydes and carboxyl functions which are readily determined by infrared spectroscopic and titrimetric means.[1] The presence of peroxide in polyamides has been detected by reacting the sample with ferrous thiocyanate in formic acid solvent,[1] but no attempt has been made to measure the level of hydroperoxides quantitatively. The colorimetric method described utilizes potassium iodide in tetrafluoropropanol, with tetrafluoropropanol also

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serving as the solvent.[5] The method is a combination and modification
of the techniques developed by Wagner et al.[6] and Heaton et al.[7] Wagner[6]
used sodium iodide in isopropanol in a titrimetric method, and in measuring
the absorbance of the liberated iodine, Heaton[7] claimed that samples
containing 0.02–5 μmoles of hydroperoxide, at a maximum concentration
of $5 \times 10^{-4}M$ will obey Beer's law.

The determination presented in this paper has a sensitivity of 1 μmole/
g. of polymer, a relative precision of less than 5%, and has been useful in
defining the dependence of the rate of peroxide formation with wavelength
of ultraviolet irradiation and the spectroscopic purity of the nylon 66 ex-
posed. The effect of heat on peroxide stability is also discussed.

EXPERIMENTAL

Instrument

A Beckman Model DU spectrophotometer equipped with 1-cm. Corex
cells was used for photometric measurements. All ultraviolet exposures
of nylon 66 yarn were conducted in the Hanou Xeno-Test.

Materials

Tetrafluoropropanol (Organic Chemicals Department, Du Pont), was
redistilled at 109°C. The reagent was prepared by shaking 2 g. of potas-
sium iodide in 100 ml. of tetrafluoropropanol in a 125–ml. glass-stoppered
Erlenmeyer flask for 10 min. Prior to use, the mixture is filtered to re-
move undissolved potassium iodide. A fresh solution should be made daily.
The calibration curve is established from a solution containing 0.32 mg. of
3.0% assayed reagent grade hydrogen peroxide per ml. of tetrafluoropro-
panol. Nylon 66 yarn having 210 filaments, each 6 den., was prepared
in the conventional commercial manner and was free from delustrant and
antioxidant.

Procedure

In constructing the calibration curve, aliquots of the peroxide solution
representing a range of 0.96–9.6 μg., were pipetted into 25-ml. volumetric
flasks, followed by 2 ml. of glacial acetic acid and 5 ml. of the reagent.
The contents was quantitatively diluted to 25 ml. and the absorbance at
400 mμ, in a 1-cm. cell, was measured after 30 min. against a blank con-
taining the solvent, reagent, and glacial acetic acid. In analyzing a sample,
0.2–0.3 g. of polymer or yarn was transferred to a 25-ml. volumetric flask,
followed by 10 ml. of solvent, and the flask was shaken in 40°C. water for
several minutes. The procedure used to establish the calibration curve
was applied to the sample. In this paper the data is reported in units of
ppm peroxide, which is defined as milligrams of peroxide as hydrogen
peroxide per 1000 g. of sample.

RESULTS AND DISCUSSION

Based on ten separate determinations, the standard deviation is equal to ± 2 at the 36 ppm range. The method has a sensitivity of about 1 μmole/g. when 1-cm. absorption cells are used. Interferences specific to nylon yarn can result from peroxides developed in yarn spin finish, as depicted in Figure 1, and from oxides of nitrogen which are readily absorbed by polyamide yarns. Samples containing delustrants must be centrifuged prior to adding the reagent.
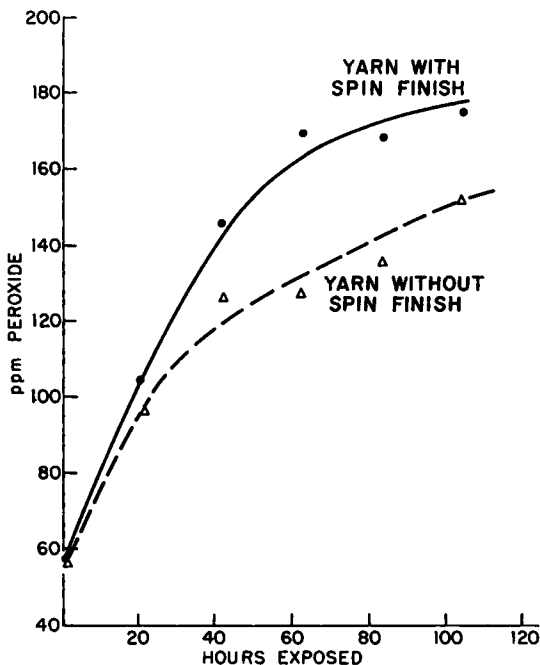

Fig. 1. Effect of spin finish on peroxide formation.

To determine the effect of irradiating ultraviolet wavelength on the rate of peroxide formation, a series of specially cut filter glasses, having different cut-off wavelengths in the ultraviolet region (Fig. 2), designed to fit over the Hanou Xeno-Test exposure panels were purchased from Dow-Corning. The nylon 66 yarns were exposed under the filters, and after specific time intervals they were sampled for peroxide content and for strength retention measurements. Figure 3 illustrates the fact that degradation of nylon 66 yarn is dependent on the wavelength of ultraviolet irradiation, with the lower wavelengths causing the greatest loss in tenacity. Correspondingly, the peroxide content can be related to the strength loss experienced by the exposed yarn (Fig. 4).

A series of samples exposed for 80 hr. were subjected to various temperatures in a vacuum oven for 15-min. intervals to determine the effect of
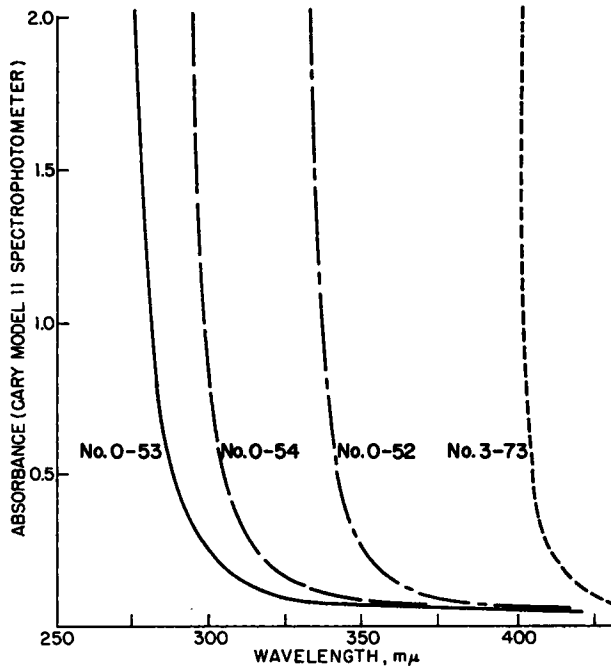
Fig. 2. Ultraviolet absorption spectra of Dow-Corning filter glass. Dimensions of glass.
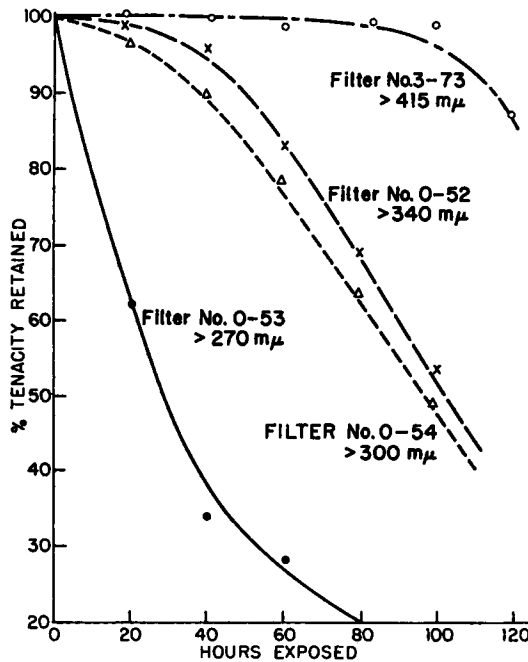12.5 × 4 cm., 2.0 mm. thick.

Fig. 3. Effect of filter glass on light durability of nylon 66 dead bright yarn. Exposure
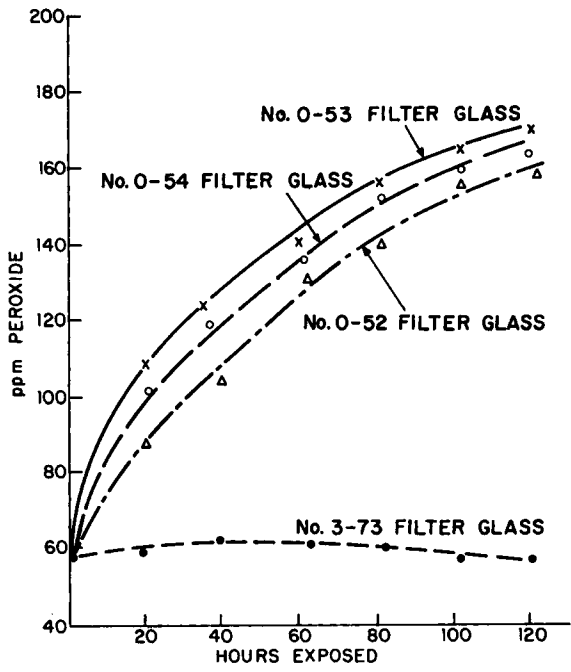instrument: Hanou Xeno-Test.

Fig. 4. Effect of filter glass on peroxide formation in nylon 66 dead bright yarn.
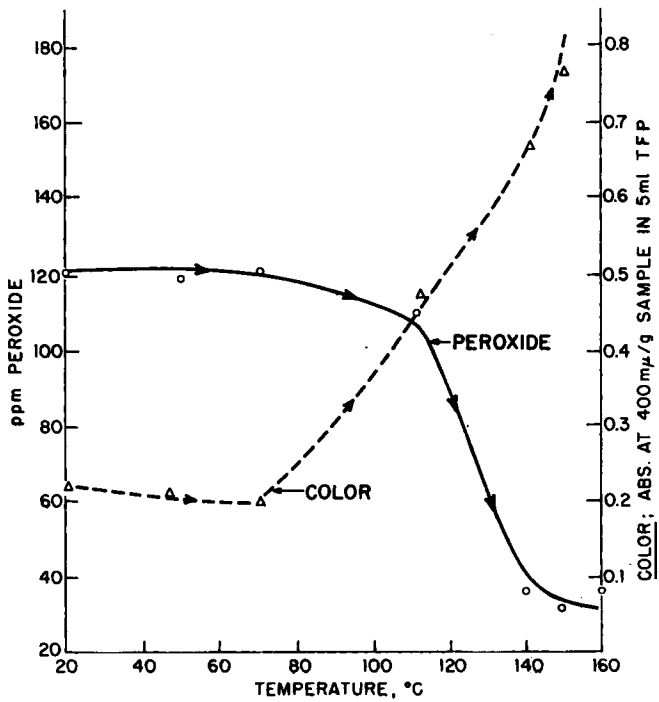

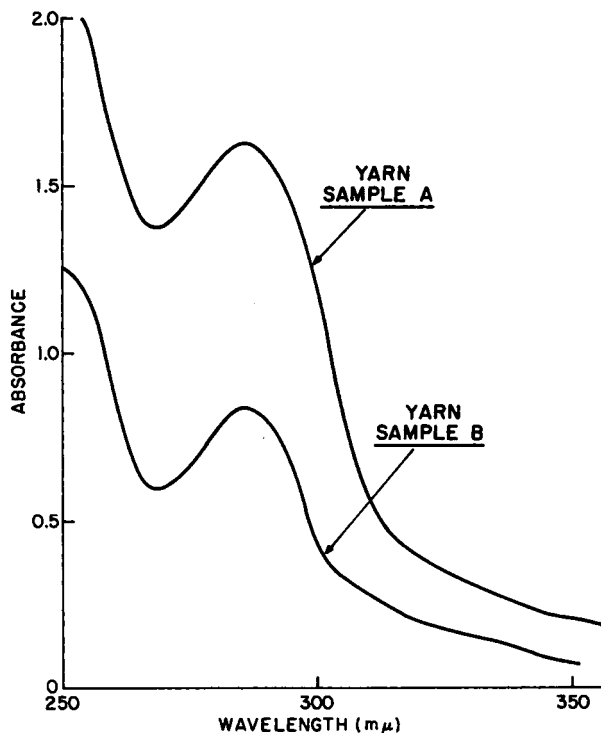Fig. 5. Effect of heat on peroxide stability and yarn color.

Fig. 6. Ultraviolet absorption spectra of nylon 66 dead bright yarn. Concentration, 2% in formic acid; cell, 1-cm., silica; instrument, Cary Model 11.

heat on peroxide stability. The results of the test, illustrated in Figure 5, show that peroxides tend to decompose at temperature greater than 100°C. Discoloration accompanies peroxide decomposition. The discoloration was measured by dissolving the sample in 5 ml. of tetrafluoropropanol and recording the absorbance at 400 mμ. The color value is reported in terms of absorbance units per gram of sample.

Photochemical decomposition mechanisms for nylon 66 show the photon attacking the amide linkage resulting in abstraction of a hydrogen atom from the carbon α to the amide NH with complete disregard to the ultraviolet absorbing properties of the sample. Commercial nylon yarns and polymers used in these studies exhibit evidence of thermal degradation when examined spectrophotometrically in the ultraviolet region. To illustrate this point, two yarns were spun from polymer having different thermal histories. This difference is evident from the spectrophotometric scans of the yarns dissolved in formic acid (Fig. 6). Both the strength retention and peroxide content of these yarns after exposure, (Figs. 7 and 8, respectively) clearly indicate that the rate of deterioration in mechanical properties for a series of nylon 66 yarns exposed under identical conditions is affected by the thermal history of the sample. In addition, the inorganic content of the yarns and polymers discussed in the earlier
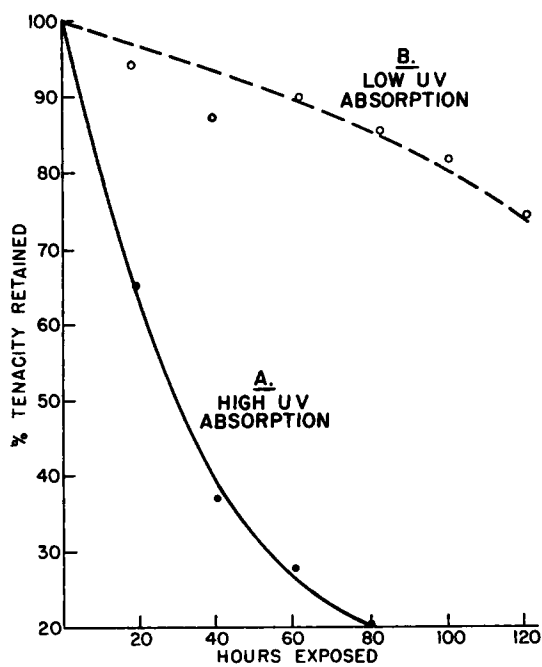
Fig. 7. Effect of thermal degradation on ultraviolet durability of nylon 66 dead bright yarn.
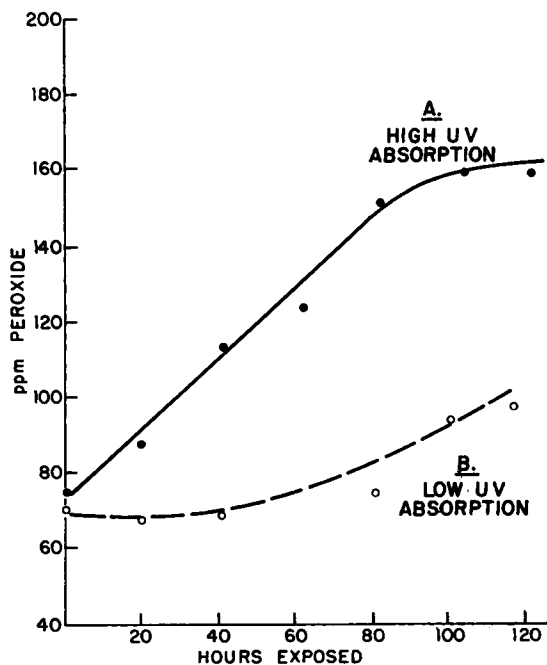

Fig. 8. Effect of thermal degradation on peroxide content of nylon 66 dead bright yarn during ultraviolet exposure.

studies were not revealed or evaluated by the authors. Traces of iron salt (10–50 ppm), readily found in the yarns used in the tests described and in commercial items can sensitize photodecomposition.

Prior to the disintegration of the polyamide chain, a primary reaction resulting from certain molecular species or inorganic complexes absorbing ultraviolet radiation and consequently triggering free radicals must be considered.

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Résumé

En accord avec les mécanismes décrits dans la littérature, la photodécomposition du nylon 66 procède par transfert de l'hydrogène situé sur le carbone α par rapport au groupe amide NH à l'aide d'un radical qui a été activé par photoabsorption. Au cours de la phase de propagation, le radical situé au carbone α peut facilement réagir avec l'oxygène atmosphérique pour former un hydroperoxyde. La formation d'un hydroperoxyde au cours du schéma de décomposition photochimique du nylon 66 a été détectée, mais n'a pas été mesurée quantitativement. A l'aide de la méthode colorimétrique décrite dans la présente publication, il est maintenant possible de déterminer le contenu en peroxydes d'un polyamide jusqu'à une concentration de l'ordre de 1 μ-mole par gramme avec une précision relative inférieure à 5%. Le polyamide est dissous dans le tétrafluoropropanol, auquel on ajoute une certaine quantité d'une solution d'iodure de potassium et d'acide acétique glacial. L'absorbance de l'iode libérée est mesurée dans une cellule de 1 cm à 400 mμ et la concentration en hydroperoxyde est déterminée à partir d'une courbe de calibrage construite à partir de solutions standards de peroxyde d'hydrogène. La vitesse de formation des peroxydes, qui dépend de la longueur d'onde du rayonnement U.V., peut être mise en relation avec la diminution de la résistance manifestée pour les fibres de nylon 66 en absence d'antioxydant et de délustrant. De plus, si l'on augmente le niveau de dégradation thermique, on accélère cette diminution de résistance des fibres ainsi que la formation des peroxydes sous l'effet de l'irradiation U.V. L'hydroperoxyde commence à se décomposer aux environs de 100°C. Le finissage des fibres contribue à la formation de peroxydes au cours de l'exposition.

Zusammenfassung

Nach dem in der Literatur angegebenen Mechanismus verläuft die photochemische Zersetzung von Nylon-66 über die Abspaltung des Wasserstoffs am α-Kohlenstoff zur Amid-NH-Gruppe durch ein freies Radikal, welches durch Lichtabsorption aktiviert wurde. In der Kettenphase kann das α-Kohlenstoffradikal leicht mit atmosphärischem Sauerstoff unter Bildung eines Hydroperoxyds reagieren. Die Bildung eines Hydroperoxyds im photochemischen Zersetzungsschema für Nylon-66 wurde zwar festgestellt, aber nicht quantitativ gemessen. Mit der in der vorliegenden Mitteilung beschriebenen kolorimetrischen Methode ist es nun möglich, den Peroxydgehalt in einem Polyamid bei einer Grössenordnung von 1 μmol pro Gramm mit einer relativen Genauigkeit von weniger als 5% zu bestimmen. Das Polyamid wird in Tetrafluoroprpanol gelöst und aliquote Teile von Kaliumjodid und Eisessiglösung zugesetzt. Die Absorbtion des

freigesetzten Jods wird in einer 1-cm-Zelle bei 400 mμ gemessen und die Hydroperoxyd-konzentration aus einer mit Wasserstoffperoxydstandardlösung erhaltenen Eichkurve bestimmt.   Die Geschwindikeit der Peroxydbildung, welche von der Wellenlänge der UV-Strahlung abhängt, kann zum Festigkeitsverlust eines Antioxydans-Delustrans-freien Nylon-66-Garnes in Beziehung gesetzt werden.   Weiters wird eine Zunahme des Ausmasses des thermischen Abbaus den Festigkeitsverlust des Garnes und die Peroxyd-bildung unter UV-Bestrahlurg beschleunigen.   Das Hydroperoxyd beginnt sich bei etwa 100°C zu zersetzen.   Das Garnfinish trägt zur Peroxydbildung während der Belichtung bei.