International Conference on

ADVANCES IN THE STABILIZATION AND CONTROLLED DEGRADATION OF POLYMERS

Volume II

International Conference on

ADVANCES IN THE STABILIZATION AND CONTROLLED DEGRADATION OF POLYMERS

Volume II

Edited by

ANGELOS V. PATSIS

Head, Chemistry Department
State University of New York
New Paltz, New York

Presented in Lucerne, Switzerland

TABLE OF CONTENTS

D. R. BAUER[1]

Photodegradation Chemistry in Thermoset Coatings and Stabilization by Hindered Amines

ABSTRACT

Photodegradation chemistries in acrylic copolymers cross-linked with melamine formaldehyde resins and isocyanate resins are compared. Particular emphasis is given to the interactions between free radical oxidation and crosslink degradation. In the case of coatings crosslinked with melamine formaldehyde resins, formaldehyde related chemistry is found to be critical. The effects of the addition of hindered amine light stabilizers on the photooxidation rates are discussed. Stabilization chemistry is followed through measurements of hindered amine and nitroxide concentrations as a function of exposure time, exposure composition, and coating composition. A model for the photostabilization chemistry of hindered amines in crosslinked coatings is presented, which attempts to account for the differences in effectiveness and permanence observed for hindered amines in melamine and urethane coatings.

KEY WORDS

Photodegradation, photostabilization, coatings, urethanes, melamine formaldehyde resins, acrylics, crosslink structure, hindered amine light stabilizer.

INTRODUCTION

Hindered amine light stabilizers are widely used to suppress photodegradation in polymers used outdoors. Most of the studies of hindered amine stabilizer mechanisms have focused on model compounds or thermoplastic polymers such as polypropylene [1-6]. Oxidation in unstabilized polypropylene is characterized by a relatively short induction period followed by rapid oxidation. The kinetic chain length can be quite long due to efficient propagation reactions down the polymer chain. The addition of hindered amines brings dramatic results. In typical accelerated ultraviolet (UV) exposures, the induction period increases from 50 to 2000 hours [6]. The basics of hindered amine stabilization is thought to involve oxidation of amine groups to nitroxides, reaction of nitroxides with radicals to form aminoethers and recycling of the aminoether back to nitroxide [7]. These reactions suppress photodegradation by interfering with free radical propagation. To account for the observed effectiveness of hindered amines in polypropylene, other factors including association of hindered amines with hydroperoxides [8,9] and excited state quenching have also been considered [10].

Although photodegradation chemistry in crosslinked coatings is also based on free radical photooxidation, the specific chemistries and kinetics are significantly different from those in polypropylene. Instead of having an induction period followed by rapid oxidation, photooxidation in coatings appears to be relatively constant in time [11]. The kinetic chain lengths are relatively short (<10). There are specific degradation chemistries which affect the crosslinked network structure, causing changes in the physical properties of the coating [12-16]. In view of the differences in degradation chemistry, it is not surprising that the addition of hindered amine to coatings will result in different stabilization effects than are observed in polypropylene. This paper summarizes differences observed in the effectiveness and permanence of one hindered amine (bis-(2,2,6,6-tetramethyl-4-piperidinyl) sebacate) as a function of coating composition and exposure variables [11,13,16]. Differences in the rate of consumption of hindered amine and in the nitroxide concentration are also discussed [17-19]. An attempt is made to account for the observed behavior on the basis of specific differences in degradation and stabilization reactions.
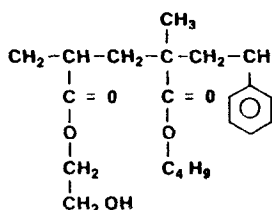
EXPERIMENTAL

Coating Materials

The coatings studied in this work consist of hydroxy functional acrylic copolymers crosslinked with a melamine formaldehyde resin or an isocyanate resin. The acrylic copolymers were prepared by conventional free
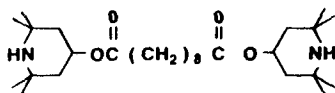
[1]Research Staff, Ford Motor Company, P.O. Box 2053, Dearborn, MI 48121.
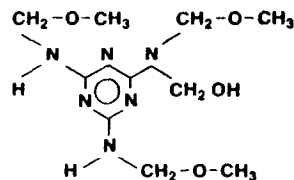
1

COATING COMPOSITION

ACRYLIC COPOLYMER

CH₃
|
CH₂-CH-CH₂-C-CH₂-CH
| |
C = 0   C = 0
| |
O   O
| |
CH₂   C₄H₉
|
CH₂OH

CROSSLINKERS

MELAMINE - FORMALDEHYDE

CH₂-O-CH₃   CH₂-O-CH₃
\   N   N   N /
H   N   N   CH₂OH
      N
H   CH₂-O-CH₃

HINDERED AMINE LIGHT STABILIZER

ISOCYANATE
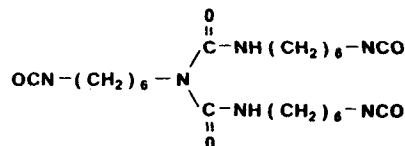
O
||
/C-NH(CH₂)₆-NCO
OCN-(CH₂)₆-N
\C-NH(CH₂)₆-NCO
||
O

Figure 1. Typical components of thermoset coatings studied.

radical copolymerization and had molecular weights ranging from 1500–8000 [20]. Most of the studies used polymers whose molecular weight was suitable for use as high solids automotive topcoats (i.e., $M_n \sim 2000$). The melamine formaldehyde resin used was a partially alkylated melamine (Cymel 325 from American Cyanamid). Coatings were formulated using a ratio of polymer to crosslinker of 70:30 and cured for 20 minutes at 130°C. The isocyanate crosslinker was a biuret of hexamethylene diisocyanate (L2291A from Mobay). The urethane coatings were formulated to obtain a 1:1 hydroxy to isocyanate ratio. No external catalysts were used. Coatings were cured for 20 minutes at 130°C. The hindered amine light stabilizer (HALS-I) was obtained from Ciba-Geiby (TIN-770) and recrystallized before use. Typical structures of the polymers, crosslinkers, and hindered amine are shown in Figure 1.

Exposure Conditions

Samples were exposed in modified Atlas UV-2 exposure chambers. The light source consisted of two FS-20 UV-A fluorescent bulbs. Light intensity was varied by the use of neutral density filters. The chambers were modified to allow independent control of air temperature and dew point [20]. The air temperature was maintained at 60°C while dew points ranged from −40°C to 50°C. A dark condensing humidity cycle was generally not employed.

Experimental Methods

Photodegradation chemistry in these coatings has been studied by infrared spectroscopy and magic angle nuclear magnetic resonance. The details of these techniques are described elsewhere [12–16]. Degradation rates were determined by following changes in band intensities with exposure time. For example, the rate of melamine crosslink scission was followed by measuring the rate of disappearance of the melamine methoxy band at 915 cm⁻¹ in the infrared. Comparisons of these rates with and without hindered amine were used to determine hindered amine effectiveness. The concentration of hindered amine was determined as a function of exposure time by extracting the hindered amine from the coating and measuring the concentration in the extract by gas chromatography [18]. The concentration of nitroxide was determined using electron spin resonance (ESR) [17,21]. Quantification details have been described elsewhere [22]. In some cases, another radical species was also observed in ESR spectra of the coating. This radical had a much different lineshape than the nitroxide and both could be quantified. The nature of the other radical component(s) is unknown though the signal is most likely due primarily to peroxy species. ESR was also used to measure the photoinitiation rates of free radicals in these coatings [23,24]. Instead of doping with a hindered amine, the coatings were doped with a persistent nitroxide and the photoinitiation rate determined from the rate of disappearance of nitroxide during photolysis. This technique will be referred to as the nitroxide decay assay to differentiate it from the HALS doping studies.
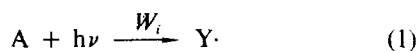
RESULTS AND DISCUSSION
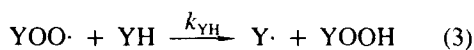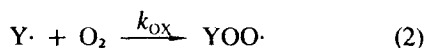
Basic Degradation and Stabilization Kinetics

As will be discussed in more detail below, photodegra-

dation chemistry in these coatings is dominated by free radical oxidation. Free radical oxidation consists of three steps: initiation, propagation and termination [25]. Hindered amines function by competing with the propagation step and thus shortening the oxidation chain length. A general scheme for the degradation and stabilization reactions are presented below:
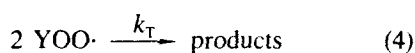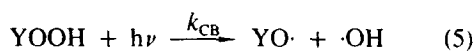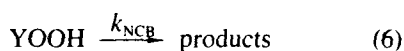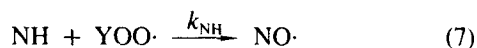
Initiation

$$A + h\nu \xrightarrow{W_i} Y\cdot \qquad (1)$$

Propagation

$$Y\cdot + O_2 \xrightarrow{k_{OX}} YOO\cdot \qquad (2)$$

$$YOO\cdot + YH \xrightarrow{k_{YH}} Y\cdot + YOOH \qquad (3)$$

Termination

$$2\ YOO\cdot \xrightarrow{k_T} products \qquad (4)$$

Chain Branching

$$YOOH + h\nu \xrightarrow{k_{CB}} YO\cdot + \cdot OH \qquad (5)$$

Hydroperoxide Decomposition

$$YOOH \xrightarrow{k_{NCB}} products \qquad (6)$$

Nitroxide Formation

$$NH + YOO\cdot \xrightarrow{k_{NH}} NO\cdot \qquad (7)$$

Nitroxide Scavenging

$$NO\cdot + Y\cdot \xrightarrow{k_{NO}} NOY \qquad (8)$$

Nitroxide Recycling

$$NOY + YOO\cdot \xrightarrow{k_{NOY}} NO\cdot \qquad (9)$$

Nitroxide Excited State Chemistry

$$NO\cdot + h\nu\ (or\ A^*) \xrightarrow{k_{EX}} NO^* \qquad (10)$$

$$NO^* + YH \xrightarrow{k_{ABS}} NOH + Y\cdot \qquad (11)$$
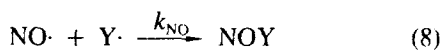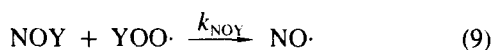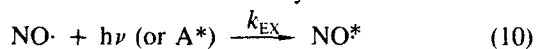
where A is a chromophore in the coating which absorbs light to form free radicals, $Y\cdot$, at a rate W_i and NH, $NO\cdot$, and NOY represent amine, nitroxide, and aminoether functionality respectively which is associated with the hindered amine. Decomposition of hydroperoxides has been discussed by Ingold [26]. Excited state nitroxides can be formed either by direct absorption [27] or by

energy transfer from another excited state species [28]. Excited state nitroxides are effective hydrogen atom abstractors [27,29].

The effectiveness of a hindered light stabilizer depends on the concentration of the different stabilizing species and on the following ratios of rate constants: k_{NH} and k_{NOY} to k_{YH} and k_{NO} to k_{OX}. The oxidation chain length is also important. In general, the longer the oxidation chain length the more likely the hindered amine will be effective. This, in part, explains why hindered amines are so effective in polypropylene. In order to derive values for the stabilization rate constants it is necessary to determine the rate constants for Reactions (1)-(7). The photoinitiation rate, W_i, can be measured directly using the nitroxide decay assay described above. This assay also provides a direct measure of the importance of nitroxide excited state chemistry [Reactions (10) and (11)]. By measuring the nitroxide decay kinetics at low nitroxide concentration, it is possible to determine the quantity k_{NO}/k_{OX} and the importance of chain branching. Combining these data with infrared spectroscopic estimates of the amount of oxidation and ESR measurements of the peroxy radical concentration yield values for k_{YH} and k_T. Typical values have been given elsewhere [19]. Chain branching is found to be unimportant since the oxidation chain lengths are relatively short and there are apparently effective means to decompose hydroperoxides in the coatings. The value of k_{NO}/k_{OX} in these coatings is roughly 0.3. This value is consistent with solution studies of the relative reactivity of nitroxide and oxygen with radicals [1]. For the exposure conditions used here, oxidation chain lengths typically ranged from 3-10. The rate constants can be expected to vary from coating to coating and may even vary with exposure conditions if the exposure conditions affect the nature of the free radical $Y\cdot$.

Coating Photodegradation Chemistry

Typical infrared spectra of undegraded and degraded acrylic/melamine and acrylic/urethane coatings are shown in Figures 2 and 3, respectively [14,16]. In both coatings there is a broadening and increase in intensity (relative to the hydrocarbon band at 2950 cm^{-1}) in the carbonyl band at 1730 cm^{-1}. This broadening is indicative of the formation of oxidation products. Difference spectra reveal a band at ~ 1700 cm^{-1}, which is likely due to formation of carboxylic acids. It is difficult to identify specific oxidation products in either the infrared or NMR spectra. The increase in area of the carbonyl band can be measured as a function of exposure time. The area increases roughly linearly with time [11]. The rate of increase is used to estimate oxidation chain lengths. The apparent lack of autocatalytic oxidation is consistent with the lack of hydroperoxide chain branching indicated by the nitroxide decay assay [19]. Thus, coating oxidation
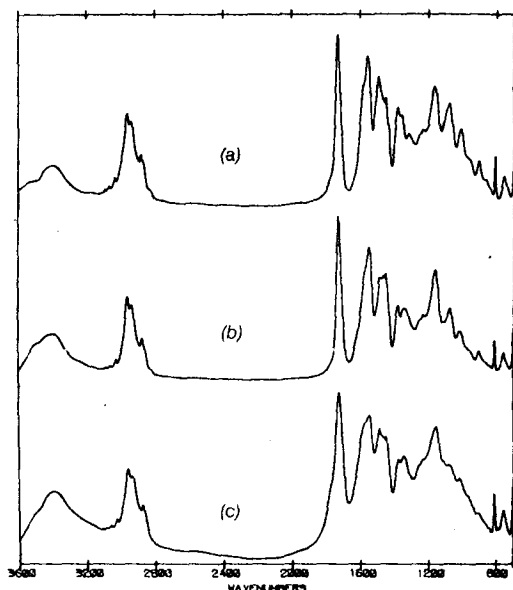
Figure 2. Infrared spectra of melamine formaldehyde crosslinked coatings. Spectra taken from unexposed sample (a); sample exposed to condensing humidity (b); and sample exposed to UV light and condensing humidity (c). Figure reprinted from [14].
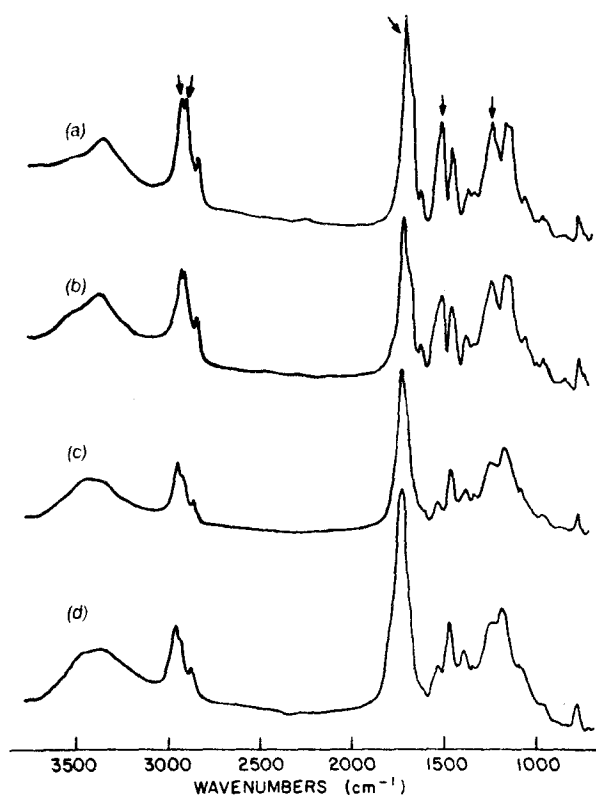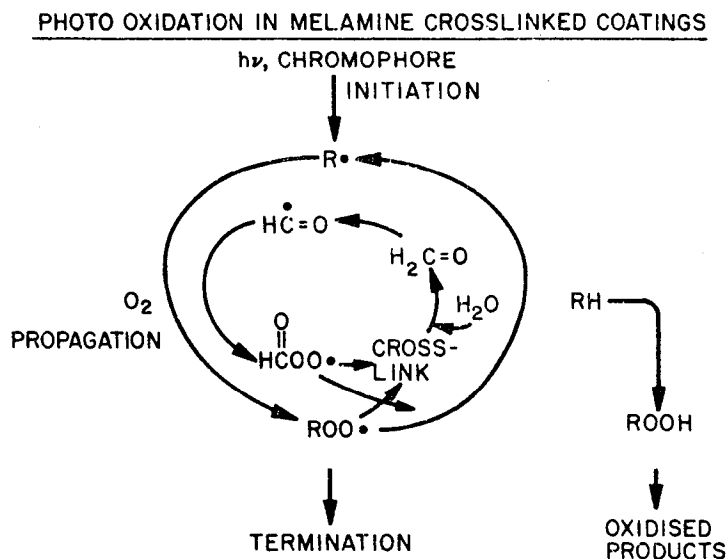

Figure 3. Infrared spectra of urethane crosslinked coatings. Spectra taken from unexposed sample (a); sample exposed to condensing humidity (b); sample exposed to UV light and condensing humidity (c); and sample exposed to UV light at a dew point of −40°C (d). Figure reprinted from [16].

kinetics are in sharp contrast to the oxidation kinetics in polypropylene. The rate of oxidation in an unstabilized melamine coating is similar (± 50%) to that in an unstabilized urethane coating if the same acrylic polymer is used. The oxidation rate in urethane coatings is found to be independent of humidity while the rate in melamine coatings increases with increasing humidity (almost doubling over the dew point range −40 to 50°C) [11,13]. From measurements of the photoinitiation rate of free radicals in these coatings, it can be concluded that the copolymer largely determines the initiation rate and that the initiation rate is independent of humidity. This suggests that the increase in oxidation observed with increasing humidity during UV exposure in melamine coatings is due to an increase in the propagation rate. A possible explanation for this effect is suggested below.

In addition to general oxidation, chemical changes which are specific to the crosslinked structure are also observed. In the urethane coating, for example, there is clear loss of the amide II and amide IV bands (at 1540 and 1240 cm^{-1}) [16]. This suggests scission of the acrylic-urethane crosslink. The scission rate is independent of humidity and thus is not a hydrolytic reaction. Scission appears to be caused by free radical attack on the urethane crosslink (possibly H-atom abstraction of one of the urethane hydrogens) [30]. For some acrylic polymers, after the urethane links are broken, the crosslinker is lost from the coating. The extent of loss of crosslinker increases somewhat with increasing exposure humidity even though the rate of scission does not.

Acrylic-melamine crosslinks are also broken during exposure to UV light and humidity. For these crosslinks, the rate of scission increases with both increasing UV light intensity and humidity during the exposure [13]. In the absence of UV light, the crosslinks undergo a slow hydrolysis [12]. The mechanism for this acid catalyzed hydrolysis has been studied [31]. When acrylic-melamine crosslinks are hydrolyzed, melamine methylol groups are formed. These methylol groups can either deformylate to amine or self-condense to form a melamine-melamine crosslink (appearance of a band at 1360 cm^{-1}) also releasing formaldehyde. Emission of formaldehyde has been observed using gas phase infrared spectroscopy [32]. Acrylic-melamine crosslinks are also broken on exposure to UV light in the absence of humidity [13]. The rate depends on light intensity and the mechanism appears to involve free radical attack on the crosslink. No melamine-melamine crosslink formation is observed suggesting that no melamine methylol groups are formed. On exposure to both UV light and humidity, the rate of crosslink scission increases to a value greater than the sum of the rates for UV light only and humidity only exposures [13]. Melamine-melamine crosslink formation is observed [14,15]. The rate of formaldehyde release is also greater in this exposure than for the UV light only or humidity only exposures [32]. A reaction scheme which

PHOTO OXIDATION IN MELAMINE CROSSLINKED COATINGS

Figure 4. Degradation chemistry of melamine crosslinked coatings.

accounts for these observations has been proposed [32]. According to this scheme, free radical attack on the crosslink forms a species which when reacted with water produces a melamine methylol group. The methylol group then can self-condense to form a melamine-melamine crosslink and release formaldehyde into the coating. Comparison of the rate of scission and the rate of formaldehyde release suggests that most of the formaldehyde formed remains in the coating. Retained formaldehyde can participate in the free radical oxidation kinetics via formation of performic acid. Peracids are strong oxidants and could account for the increase in oxidation with humidity observed in the melamine coating. A schematic picture of the interaction of humidity, formaldehyde, and UV light in the degradation of melamine cross-linked coatings is shown in Figure 4.

Effectiveness of Hindered Amines

Experimentally, the effectiveness of a hindered amine light stabilizer can be measured by comparing the degradation rates with and without hindered amine. In typical high solids acrylic/melamine coatings, the addition of 2% by weight hindered amine reduces the oxidation and acrylic-melamine crosslink scission rate by a factor of about 2 [11,13]. In acrylic/urethane coatings, the effects are much more dramatic [30]. The oxidation rate can be reduced by factors of 5–10 while the acrylic-urethane crosslink scission rate can be reduced by factors of 10–20, Figure 5. The rate of oxidation in acrylic/urethane coatings appears to be reduced almost to the level of the photoinitiation rate (i.e., an oxidation chain length of 1). The effectiveness of hindered amines in these coatings appears to be roughly constant for long periods of expo-

sure time. This constant effectiveness and the big difference in effectiveness between urethane and melamine coatings is not easy to explain. In the sections that follow, studies of HALS chemistry will be presented which are aimed at understanding the chemistry underlying these observations and at interpreting these observations in terms of changes in the different stabilization rate constants. Formaldehyde chemistry will play a key role in these discussions.

Rate of HALS Consumption

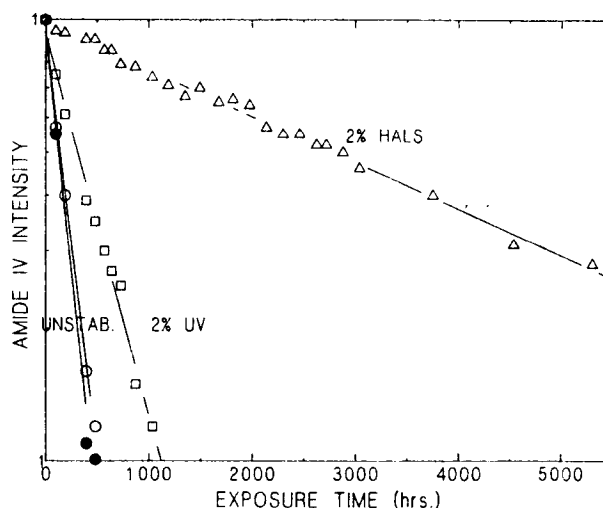According to Reaction (7), hindered amine functionality is consumed at a rate determined by k_{NH} and the

Figure 5. Effect of HALS I on rate of loss of Amide II signal in an acrylic/urethane coating. Figure reprinted from [30].
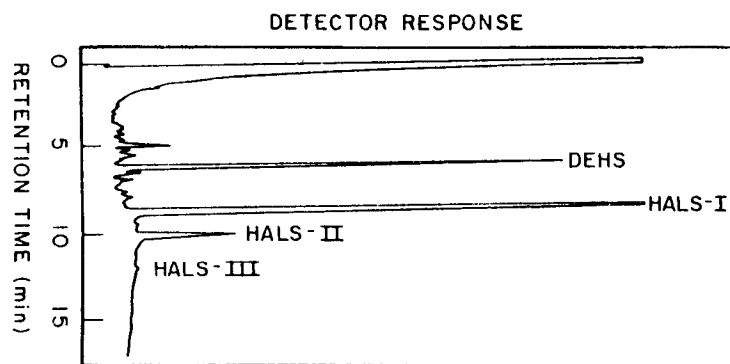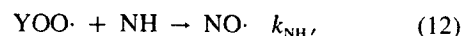
DETECTOR RESPONSE

Figure 6. Gas chromatogram from extracts of cured acrylic/melamine coating. Figure reprinted from [18].

steady state concentration of YOO·. The peroxy radical concentration can be measured using ESR. Thus, in principle k_{NH} can be determined from measurements of the loss of amine functionality. A gas chromatography technique to determine the amine concentration has been described and a typical gas chromatogram of an extract from a cured acrylic/melamine coating is shown in Figure 6 [18]. In addition to the signal from HALS I, two weaker signals are observed which can be assigned to the mono- and di-N-methylated versions of HALS I. Approximately 15% of the NH groups are converted to $N-CH_3$ groups during cure of the melamine coating. This reaction does not occur in the urethane coating. This observation can be explained by the fact that formaldehyde is released during the cure of melamine coatings. Formaldehyde is a known methylating agent for secondary amines [33]. There is more than enough formaldehyde released during melamine crosslinking to account for the observed methylation.
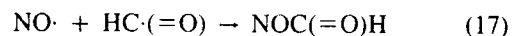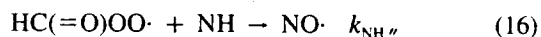
The concentration of HALS I (and the other hindered amines) has been measured as a function of exposure time for both a melamine and urethane crosslinked acrylic copolymer doped with 2% by weight HALS I at different light intensities and humidities [18]. The photoinitiation rate of free radicals for both coatings at the maximum light intensity used was 12×10^{-8} mole/g·min. The oxidation chain length was ~3–5. At this intensity, the initial rate of consumption of NH functionality was 0.78×10^{-8} mole/g·min for the urethane coating independent of humidity. The initial rate for melamine coating was 1.35×10^{-8} mole/g·min at a dew point of $-40°C$ and 0.59×10^{-8} mole/g·min at a dew point of $25°C$. In the urethane coating NH functionality is lost steadily with almost 75% consumed by 140 hours of exposure. In the melamine coating under dry exposure the consumption of NH and $N-CH_3$ groups is even more rapid with roughly 90% of the NH groups consumed by 140 hours. The rate of loss of NH functionality is roughly proportional to the square root of the light intensity. The behavior in the melamine coating is quite different under humid exposures. The concentration of

NH groups drops 40% in the first 40 hours then remains roughly constant out to over 300 hours. The $N-CH_3$ concentration actually increases initially then parallels the NH concentration. The fact that the NH concentration reaches a plateau value suggests that some mechanism exists to recycle nitroxide or aminoethers back to NH groups. The observed behavior can be accounted for by the following reaction scheme:

Urethane Coating

$$YOO· + NH \rightarrow NO· \quad k_{NH'} \qquad (12)$$

Melamine Coating

$$H_2C=O + YOO· \rightarrow HC·(=O) \qquad (13)$$

$$HC·(=O) + O_2 \rightarrow HC(=O)OO· \qquad (14)$$

$$YOO· + NH \rightarrow NO· \quad k_{NH'} \qquad (15)$$

$$HC(=O)OO· + NH \rightarrow NO· \quad k_{NH''} \qquad (16)$$

$$NO· + HC·(=O) \rightarrow NOC(=O)H \qquad (17)$$

$$NOC(=O)H \rightarrow NH + CO_2 \quad k_{RE} \qquad (18)$$
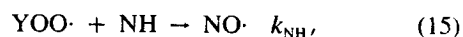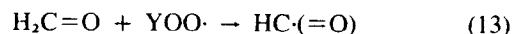
(note: water is required as a proton transfer agent, see [18])

$$NH + H_2C=O \rightarrow N-CH_3 \qquad (19)$$
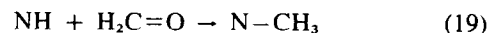
In the urethane case, the initial rate of NH consumption is $k_{NH'}$ [NH] [YOO·]. The measured rate k_{NH} is equal to $k_{NH'}$. In the case of the melamine under dry conditions the rate is $k_{NH'}$ [NH] [YOO·] + $k_{NH''}$ [NH] [HC(=O)OO·]. The measured rate constant k_{NH} in the melamine coating will be a weighted average of $k_{NH'}$ and $k_{NH''}$. The total radical concentration is similar in the melamine and urethane coating. Peracids are much stronger oxidants of NH groups than are peroxy radicals [3]. Thus, $k_{NH''} > k_{NH'}$ and the rate of consumption of

NH groups is greater in the melamine coating under dry conditions than it is in the urethane coating. Under humid conditions, however, the recycling reaction [Reaction (18)] occurs and the consumption rate of amine is reduced by the quantity k_{RE} [NOC(=O)H]. Thus, the rate of consumption of NH groups can decrease even though the amount of formaldehyde released increases. When recycling occurs, it is not possible to determine k_{NH} from the amine consumption data. A determination of k_{NH} using the initial rate of formation of nitroxide will be given below. Formaldehyde released in the melamine coating on exposure also accounts for the high level of $N-CH_3$ functionality maintained in this coating [Reaction (19)].

Although clear differences in the conversion of hindered amine to nitroxide can be observed in the different coatings, the overall effect of these differences on the effectiveness of the stabilizer may be small. $N-CH_3$ groups and NH groups are converted to nitroxide at a similar rate. In all cases the conversion of NH groups to nitroxide is inefficient relative to the photoinitiation rate or oxidation rate (i.e., the ratio k_{NH} [NH]/k_{YH} [YH] is small). Thus, Reaction (7) can not be responsible for the observed reduction in oxidation chain length observed in these coatings.

Nitroxide Concentration Studies

Since Reaction (7) is not the main stabilizing reaction, it is necessary to study Reactions (8) and (9) which involve nitroxides and aminoethers. It is not possible to quantify the aminoether compositions and concentration in crosslinked coatings. The nitroxide concentration, on the other hand, can be quantified [21,22]. As shown in Figure 7, the concentration of nitroxide in hindered amine doped coatings increases to a maximum value then slowly decreases [17]. There is a small level of nitroxide present just after cure of these coatings. The concentration of nitroxide in the coating is a complex balance of formation from amine, consumption by reaction with radicals, and regeneration from aminoethers. It does not appear to be feasible to develop a model to predict the detailed time dependence of the nitroxide concentration. Several parameters can be determined from curves such as in Figure 7, including the initial net nitroxide formation rate, the nitroxide maximum and time to maximum, and the net rate of loss of nitroxide at long times. Although these parameters vary depending on the copolymer, none of the parameters appear to correlate directly either with oxidation rate or with stabilizer effectiveness. It is possible to use these parameters in conjunction with other data to derive values of the different stabilization rate constants.

The initial net nitroxide formation rates are given for the melamine and urethane coatings used in the hindered amine consumption study in Table 1 [17–19]. Also given
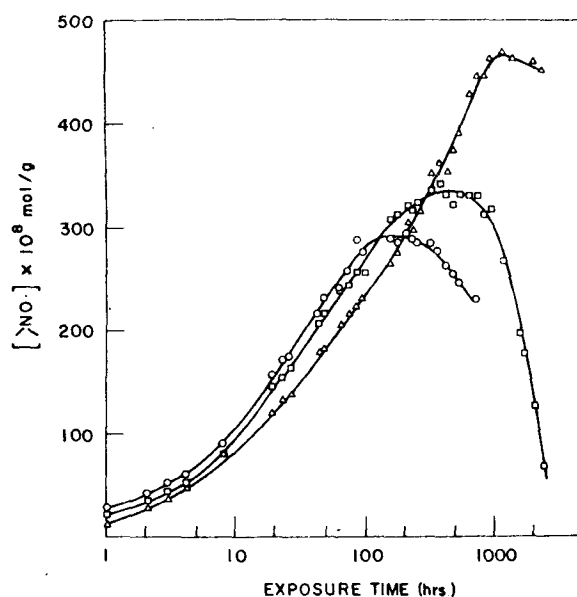
Figure 7. Nitroxide concentration versus exposure time and light intensity for an acrylic/melamine coating. Figure reprinted from [17].

are the photoinitiation rates and the initial NH consumption rates. The following points can be made: The initial net nitroxide formation rate is much smaller than either the photoinitiation rate or the initial hindered amine consumption rate; the initial net nitroxide formation rate is a strong function of coating composition and (in the case of the melamine coating) exposure humidity but is only a weak function of light intensity; higher amine consumption rates do not necessarily mean higher nitroxide formation rates. Initially, the net nitroxide formation rate (d[NO·]/dt) can be written in terms of Reactions (7), (8), (10), and (11). Nitroxide regeneration, Reaction (9),

Table 1. Comparison on photoinitiation rates, nitroxide formation rates, and hindered amine consumption rates. *

Dew Point	PIR**	d[NO·]/dt		$-d$[NH]/dt	
		Expt'l.	Pred.	Expt'l.	Pred.
Acrylic/Urethane:					
−40°C	12	0.012	0.014	0.78	0.71
25°C	12	0.016	0.014	0.78	0.71
Acrylic/Melamine:					
−40°C	12	0.095	0.06	1.35	1.39
−40°C	7	0.092	0.12	0.95	1.04
−40°C	1.4	0.068	0.105	0.55	0.42
25°C	12	0.24	0.25	0.5	2.42†
25°C	7	0.18	0.26		
25°C	1.4	0.14	0.16		

* All data from [18].
** Photoinitiation rate of free radicals. All rates × 10⁸ mole/g·min.
† Ignores hindered amine recycling reaction. See text.

can be ignored since the concentration of aminoether is small. The rates of nitroxide consumption resulting from nitroxide scavenging [Reaction (8)] and nitroxide excited state chemistry [Reactions (10) and (11)] can be calculated as discussed above and in more detail in [19]. Adding these rates to the measured net formation rates in Table 1 yield values for the rate of amine consumption, Reaction (7), and thus values for k_{NH}. The amine consumption rates calculated from the nitroxide data can be compared to the values measured in the amine consumption experiment. The dependence of nitroxide formation on light intensity can also be calculated. The calculated values are also given in Table 1. In general the agreement is quite good considering the approximations used in the analysis. The predicted value for NH consumption for the melamine coating under humid conditions is high since the recycling reaction [k_{RE}-Reaction (19)] is ignored. As expected from the arguments presented in the previous section, the rate constant k_{NH} is larger for the melamine coatings than for the urethane coating and increases with increasing humidity for the melamine coating [19].

The dependence on light intensity deserves further comment. In general, in oxidation reactions, the radical concentration depends on the square root of the light intensity. Thus it might be expected that the net nitroxide formation rate would increase with the square root of the photoinitiation rate similar to the amine consumption rate. Instead, there is very little dependence on light intensity. This result is due to the contribution of Reactions (10) and (11) to the equation for nitroxide consumption. The amount of nitroxide consumed due to nitroxide excited state chemistry is directly proportional to light intensity. Thus, the net formation rate becomes a complicated function of light intensity. The model predicts the observed behavior reasonably well.

The nitroxide concentrations in these coatings rise steadily to a maximum value and then slowly decrease. The nitroxide concentration reaches a maximum roughly when the hindered amine concentration is depleted (or has reached its plateau value). Maximum nitroxide concentrations in coatings doped with 2% by weight HALS I range from 150–400 × 10^{-8} mole/g for melamine coatings [11,17]. The values are similar though generally

somewhat lower for urethane coatings [30]. In both cases, the maximum nitroxide concentration increases with decreasing light intensity. The difference observed in effectiveness between melamine and urethane coatings can not be due simply to differences in nitroxide concentration. Using Reactions (1)–(11), the following expression can be written for the maximum nitroxide concentration [19]:

$$[NO \cdot]_{max} = \frac{(k_{NH}[NH] + k_{NOY}[NOY])[YOO \cdot]}{k_{NO}[Y \cdot] + C}$$

where C is a measure of the rate of hydrogen atom abstraction by excited state nitroxide [Reactions (10) and (11)]. The values of C, k_{NO}, k_{NH}, [Y·], and [YOO·] can be determined by the methods described above. Comparing the time to reach the maximum nitroxide concentration with the hindered amine consumption experiments yields a value for [NH]. The concentration of aminoether can be estimated by mass balance (i.e., [NOY](t) = [NH](0) − [NH](t) − [NO·](t)). Assuming that none of the rate constants change with time, it is possible to derive values for k_{NOY} from the measured values of [NO·]$_{max}$ [17,30]. For the urethane coating it is found that k_{NOY} is roughly 100 times larger than k_{NH}. The predicted reduction in the oxidation chain length is large and is consistent with previously measured values [16,30]. Thus, Reactions (8) and (9) are primarily responsible for HALS stabilization in urethane coatings. The results for melamine coatings are more complicated. Holding the other rate constants fixed yields a value of k_{NOY} similar to that in the urethane coating. This results in a reduction in the oxidation chain length that is much larger than is observed experimentally [11,13]. To account for the observed HALS I effectiveness and the nitroxide concentration maximum in the melamine coating it is necessary that the value of k_{NOY} be roughly 10 times larger than k_{NH} and that the value of the ratio of k_{NO} to k_{OX} drop by about a factor of 4–5 from its initial value. The differences in the behavior of the stabilization rate constants in the melamine and urethane coatings is summarized in Table 2. Although the reaction scheme does account for the ob-

Table 2. Effect of composition and humidity on stabilization rate constants.

k_{NH}	Urethane (Dry) = Urethane (Humid) < Melamine (Dry) < Melamine (Humid). Approximate relative rates: 1:1:2:3.
k_{NO} (initial)	Urethane = Melamine, independent of humidity.
$k_{NO}(t)/k_{OX}(t)$	This ratio is independent of time in Urethanes. In melamines the ratio decreases by factor of 4–5.
k_{NOY}	Urethane > Melamine (wet) > Melamine (dry). Approximate relative rates: 5:2:1.
k_{NOY}/k_{NH}	Urethane ~100; Melamine ~10.
$\dfrac{k_{NH}[NH]}{k_{YH}[YH]}$	~0.02–0.04 for both urethane and melamine coatings studied.
$\dfrac{k_{NOY}[NOY]}{k_{YH}[YH]}$	Urethane ~1.5; Melamine ~0.4

served nitroxide concentration maximum and the observed reduction in oxidation chain length, it does not predict the observed increase in nitroxide maximum with decreasing light intensity. The reason for this behavior is unclear at present.

Explanations for the variations summarized in Table 2 are at this point speculative. The observation that k_{NOY} is much greater than k_{NH} is at odds with model compound studies for polypropylene which suggested that they were comparable [2]. The reactivity of aminoether species clearly depends both on the composition of the aminoether and attacking radical. Apparently the compositions are significantly different in coatings from the model compounds studied. The observed differences between the melamine and urethane coatings can be explained in part at least by invoking formaldehyde based chemistry. Initially, nitroxides are scavenging radicals formed by primary photochemistry. These processes are the same in melamine and urethane coatings. In the melamine coating the formation of $HC\cdot(=O)$ may change the balance between Reactions (2) and (8). This could account for the apparent decrease in the value of k_{NO}/k_{OX} with time. Differences in radical reactivity with nitroxide and oxygen have been reported in solution [1]. The lower value of k_{NOY} in the melamine coatings may result from a lack of an efficient way to convert $NO-C(=O)H$ back to nitroxide. In this regard, it is interesting to note that $NOC(=O)CH_3$ is not as effective a photostabilizer in polypropylene as are species such as $NO-C_4H_9$ [6]. Reaction (19), which recycles $NO-C(=O)H$ to NH, does not contribute directly to photostabilization since it does not consume free radicals. It produces NH groups whose stabilizing activity is not as great as $NO\cdot$ or other NOY groups.

So far none of the reactions mentioned irreversibly consume stabilizer. As shown in Figure 7, there is in general a slow loss of nitroxide. Surprisingly, the effectiveness of the HALS additive does not change much until the nitroxide drops to a very low value. Apparently much of the change in nitroxide concentration over this time period reflects a change in balance between the nitroxide and aminoether reactions, which may not change the overall effectiveness. When the nitroxide drops to a low level ($\sim 10 \times 10^{-8}$ mole/g), the peroxy radicals seen initially reappear, suggesting that the stabilizer is no longer effective. The exposure time required to "consume" the stabilizer depends on the coating type and on the exposure conditions. Stabilizer lifetime is shorter in coatings with high photoinitiation rates; i is longer in urethane coatings than in melamine coatings; it is roughly inversely proportional to light intensity; and it is under humid exposures longer than under dry exposures. The chemistries responsible for the depletion of stabilizer activity are unknown. Since stabilizer permanence is just as important to coating performance as stabilizer effectiveness, it is clear that coating performance should be an active area of research for years to come.

CONCLUSION

This paper summarizes studies of photodegradation in thermoset organic coatings and their stabilization by hindered amines. While much has been learned about the chemistry and kinetics of degradation and stabilization, there remain many unanswered questions. The following list is merely suggestive of the many areas of research that could be pursued:

1. Is formaldehyde based chemistry responsible for all the observed differences between melamine and urethane coatings?
2. What reactions are responsible for the slow decrease in nitroxide concentration and the ultimate loss of stabilizer effectiveness?
3. Specifically, why does humidity affect stabilizer permanence?
4. What are the structures of the aminoether species formed in thermoset coatings?
5. How does initial HALS structure influence overall stabilizer reactivity and permanence?
6. Is stabilizer migration important?
7. Are other stabilization mechanisms (e.g., quenching, specific association with or decomposition of chromophores) important in coatings?

REFERENCES

1. Brownlie, I. T. and K. U. Ingold. *Can. J. Chem.*, 45:2427 (1967).
2. Grattan, D. W., D. J. Carlsson and D. M. Wiles. *Poly. Deg. Stab.*, 1:69 (1979).
3. Felder, B., R. Schumacher and F. Sitek. *Helv. Chim. Acta*, 63:132 (1980).
4. Shilov, Yu. B. and E. T. Denisov. *Polym. Sci. USSR*, 20:2079 (1979).
5. Carlsson, D. J., A. Garton and D. M. Wiles. In *Developments in Polymer Stabilization, Vol. I*. G. Scott, ed. London:Applied Science Pub., p. 219 (1979).
6. Kurumada, T., H. Ohsawa, T. Fujita and T. Toda. *J. Polym. Sci., Polym. Chem.*, 22:277 (1984).
7. Scott, G. *J. Photochem.*, 25:83 (1984).
8. Chan, K. H., D. J. Carlsson and D. M. Wiles. *J. Polym. Sci., Polym. Lett.*, 18:607 (1980).
9. Carlsson, D. J., K. H. Chan, J. Durmis and D. M. Wiles. *J. Polym. Sci., Polym. Chem.*, 20:575 (1982).
10. Bortolus, P., S. Dellonte, A. Faucitano and F. Gratani. *Macromolecules*, 19:2916 (1986).
11. Gerlock, J. L., D. R. Bauer and L. M. Briggs. In *Polymer Stabilization and Degradation*. P. Klemchuk, ed. ACS Symposium Series No. 280, Washington, DC, p. 119 (1985).
12. Bauer, D. R. *J. Appl. Polym. Sci.*, 27:3651 (1982).
13. Bauer, D. R. and L. M. Briggs. In *Characterization of Highly Crosslinked Polymers*. S. S. Labana and R. A. Dickie, eds. ACS Symposium Series No. 243, Washington, DC, p. 271 (1984).

14. Bauer, D. R., R. A. Dickie and J. L. Koenig. *J. Polym. Sci., Polym. Phys.*, 22:2009 (1984).

15. Bauer, D. R., R. A. Dickie and J. L. Koenig. *Ind. Eng. Chem., Prod. Res. Dev.*, 24:121 (1985).

16. Bauer, D. R., R. A. Dickie and J. L. Koenig. *Ind. Eng. Chem., Prod. Res. Dev.*, 25:289 (1986).

17. Gerlock, J. L., D. R. Bauer and L. M. Briggs. *Polym. Deg. Stab.*, 14:53 (1986).

18. Gerlock, J. L., T. Riley and D. R. Bauer. *Polym. Deg. Stab.*, 14:73 (1986).

19. Bauer, D. R. and J. L. Gerlock. *Polym. Deg. Stab.*, 14:97 (1986).

20. Gerlock, J. L., D. R. Bauer and L. M. Briggs. In *Characterization of Highly Crosslinked Polymers*. S. S. Labana and R. A. Dickie, eds. ACS Symposium Series No. 243, Washington, DC, p. 285 (1984).

21. Gerlock, J. L., H. van Oene and D. R. Bauer. *Euro. Polym. J.*, 19:11 (1983).

22. Gerlock, J. L. *J. Anal. Chem.*, 55:1520 (1983).

23. Gerlock, J. L. and D. R. Bauer. *J. Polym. Sci., Polym. Lett.*, 22:447 (1984).

24. Gerlock, J. L., D. R. Bauer, L. M. Briggs and R. A. Dickie. *J. Coat. Technol.*, 57(722):37 (1985).

25. Emanuel, N. M., E. T. Denisov and Z. K. Maizus. *Liquid Phase Oxidation of Hydrocarbons*. New York:Plenum Press (1967).

26. Ingold, K. U. *Chem. Rev.*, 61:563 (1961).

27. Bogatryeva, A. I. and A. L. Buchachenko. *Kinetics and Catalysis*, 12:1226 (1971).

28. Bauer, D. R., L. M. Briggs and J. L. Gerlock. *J. Polym. Sci., Polym. Phys.*, 24:1651 (1986).

29. Keana, J. F. W., R. Dinerstein and F. Baitis. *J. Org. Chem.*, 36:209 (1971).

30. Bauer, D. R., M. J. Dean and J. L. Gerlock. *Ind. Eng. Chem.* (submitted).

31. Berge, A., B. Kvaeven and J. Ugelstad. *Euro. Polym. J.*, 6:981 (1970).

32. Gerlock, J. L., M. J. Dean, T. J. Korniski and D. R. Bauer. *Ind. Eng. Chem., Prod. Res. Dev.*, 25:446 (1986).

33. Moore, M. L. In *Organic Reactions, Vol. 5*. R. Adams, ed. New York:John Wiley & Sons, chapter 7, p. 307 (1949).

N. C. Billingham[1]
J. W. Burdon[1]
I. W. Kaluska[2]
E. S. O'Keefe[1]
E. T. H. Then[1]

Chemiluminescence from Oxidative Degradation of Polymers

ABSTRACT

Studies of the ultra-weak chemiluminescence which accompanies polymer oxidation are shown to provide an extremely sensitive way of monitoring degradation. It is shown that luminescence can be observed not only during polymer oxidation but also when samples are heated in an inert atmosphere. Both types of luminescence have been studied for the oxidation of natural rubber and Nylon 6.6 and for the electron beam irradiation of Nylon 6.6 and of polyethylene. In unirradiated samples the luminescence can be correlated with the peroxidation of the polymer although rather different mechanisms of luminescence are involved in rubbers and in Nylon. The luminescence of irradiated polymers is shown to be more complex and probably involves more than one mechanism.

KEY WORDS

Chemiluminescence, oxyluminescence, polymer oxidation, polymer irradiation, natural rubber, Nylon 6.6, polyethylene.

INTRODUCTION

After many years of research there is general agreement about the chemistry of the reactions which lead to peroxidation, chain scission and embrittlement in polymers and many effective stabilizers have been developed. There remains, however, a number of problems. In particular, the prediction of polymer lifetimes is still a challenge, based mostly on extrapolations of accelerated aging tests. The problem is that although we know what reactions are involved in the degradation sequence, almost all of our knowledge of their kinetics is derived from studies of reactions in the liquid phase and we know rather little of how the polymer matrix affects the reactions. The difficulty is that the reaction rates are very low, so that the concentrations of the intermediate free-radicals are too small for measurement by any of the conventional methods, as are the concentrations of stable intermediates. Although progress has been made, it has mostly involved studies of γ-initiated oxidation where the radical concentrations are much higher than normal. There is a clear and established need for more sensitive techniques for probing oxidation. One possibility is the measurement of the associated light emission.

The emission of very low levels of light ("oxyluminescence"), which accompanies the oxidation of all organic materials, has been known and well documented for many years [1,2]. The first application of oxyluminescence measurements to polymers was reported in 1961 by Ashby [3], who showed that many polymers emit light very weakly when they are heated to around 180°C in air and that the emission is associated with oxidation. He showed that luminescence is most intense from polymers containing amide groups (Nylon and polyurethanes) and least intense from hydrocarbon polymers. The total amount of light emitted was found to be proportional to the concentration of carbonyl groups developed in the polymer, although at least 10^4 carbonyl groups were estimated to be formed per photon emitted. Ashby also showed that the luminescence is suppressed or reduced by antioxidants and proposed its measurement as a technique for evaluation of antioxidants. Similar studies of polymers were reported by Schard and Russell [4,5], who also demonstrated the connection between luminescence and oxidation. These early studies were limited by the low signal to noise ratio of analogue electrometers so that oxidation could be observed only at high temperatures, where other techniques are easier to use and provide more direct results. In recent years, the development of fast single-photon counters has enabled low light levels to be measured with much greater sensitivity and there has been new interest in oxyluminescence.

One problem in the interpretation of luminescence data has been that there is no general agreement on the origin of the luminescence. The requirements for a reaction to lead to luminescence are quite restrictive, in that the product must be formed in an excited state, with sufficient energy to emit a detectable photon and a finite prob-

ability of decay to the ground state via light emission, rather than radiationless deactivation. The intensity of oxyluminescence is too low for it to be measurable when dispersed by a high-resolution monochromator, but simple experiments with filters have suggested that the emission from Nylon has a peak above 350 nm, similar to the phosphorescence of an excited carbonyl group [6]. This emission requires the luminescent reaction to have an energy yield of at least 300 kJ mol^{-1}, which implies either a highly exothermic reaction or one with a high activation energy. It is generally accepted that the emission comes from phosphorescence of an excited ketone, but opinions differ on the origin of the ketone. Many workers [2,5,6] have proposed that it is produced in the termination reaction of two secondary alkyl-peroxy radicals via the mechanism:

$$RO_2^{\cdot} \ + \ \underset{R}{\overset{R}{>}}CH-O_2^{\cdot} \ \longrightarrow \ ROH \ + \ ^1O_2 + \underset{R}{\overset{R}{>}}C=O$$
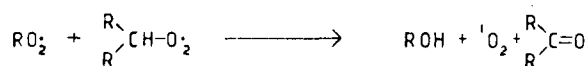
This model seems to work well for liquid phase oxidation and has been used widely. For example, Mendenhall et al. [7] claimed that low-temperature luminescence measurements could be interpreted by kinetic models based on this mechanism and could be useful for a wide variety of substrates, including aviation fuels and food oils as well as polymers.

In contrast, other workers [8] have suggested that the luminescence is produced by the decomposition of the polymer hydroperoxide. Simple unimolecular decomposition is not sufficiently exoenergetic to allow luminescence and it must arise either from a molecular rearrangement reaction [9] or from a two stage process in which primary radicals, produced by decomposition of peroxides, disproportionate within the cage in which they are produced [10]:

$$H-C-OOH \ \underset{H-C-O\cdot \ + \ \cdot OH}{\overset{\diagup}{\diagdown}} \ \overset{\diagup}{\underset{\diagup}{\longrightarrow}} \ C=O \ + \ H_2O$$
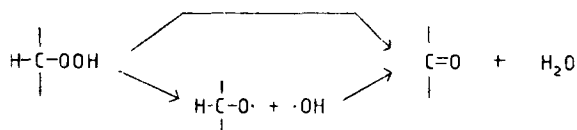
The distinction between these two mechanisms is essentially semantic but it should be noted that neither pathway requires oxygen to be present.

Zlatkevich [11] has used this model to interpret measurements of oxyluminescence and claims to be able to make lifetime predictions. Recently, Mendenhall and Quinga [13] pointed out that the disproportionation of alkoxy radicals can give luminescence with high quantum efficiency and suggested that this reaction might play a part in the oxyluminescence from polymers. This mechanism is very similar to that proposed for peroxide decomposition, with the exception that the radicals involved are not primary radicals. It is important to recognise that the rates of initiation and termination are ex-

pected to be equal in the steady-state conditions used in most studies so that mechanisms involving peroxide decomposition (initiation) may not be kinetically distinguishable from those involving radical recombination (termination).

Some elegant work has been reported by George, who has reviewed his contribution [6]. He assumes that luminescence arises from chain termination and uses this model to interpret the results of experiments (pioneered by Shlyapintokh et al. [1] for liquids), in which the sample is perturbed by a sudden change in either temperature or atmosphere and its return to steady-state conditions is monitored. He interpreted results for Nylon 6.6 in terms of the relative rate constants for mutual termination of alkyl (in the absence of oxygen) and alkyl-peroxy (upon oxygen admission) reactions, assuming a constant rate of initiation from the decomposition of adventitious peroxides. The work was all carried out on commercial Nylon fibres, which had been extracted to remove stabilizers. Complete removal of the stabilizer from a highly drawn fibre is almost impossible and radical mobilities in highly drawn fibres may be very much more restricted than in unstressed materials so that there is some query as to how far these conclusions can be generalised to other polymers or even to unoriented Nylon.

Clearly if chemiluminescence measurements on polymers are to be placed on a quantitative basis, it is desirable to have a better understanding of the mechanisms of luminescence and how they relate to the overall oxidation sequence. With this desire in mind we have been studying luminescence from a variety of polymers. We here report some of the phenomena which can be observed in three different systems of increasing complexity—the autoxidation of natural rubber, the autoxidation of Nylon 6.6 and the electron beam irradiation of Nylon and polyethylene.

EXPERIMENTAL

Photon Counting

Oxyluminescence emission from polymers under conditions approximating end use is extremely weak, often less than 100 photons per second reaching the detector in a typical experimental geometry. This observation means that very sensitive detection is needed. We infer that the use of a cooled photomultiplier as detector and an efficient pulse analyser is needed to carry out the photon counting. The instrument which we use was developed in our own laboratory using a micro-computer to carry out the photon counting and also to control the temperature of the sample and the gas flow over it. Full details of the instrument have been given elsewhere [14]. The sample is usually in the form of a thin film with dimensions of around 2.5 cm square. Whilst there is no objection to thick samples, thin ones give better temperature control

and reduce the risk of diffusion control effects. We have recently modified the equipment to allow monitoring of luminescence response following irradiation of the sample with UV light and to allow measurements of the emission spectra of luminescence using a computer controlled linear interference filter.

Polymer Samples

Natural rubber was a sample of Sri-Lankan pale crepe rubber, purified by repeated reprecipitations to remove proteins and natural antioxidants. Samples were prepared for luminescence measurements by casting from toluene solution onto clean aluminum pans. Nylon 6.6 was additive-free, melt extruded, unoriented film. Polyethylene was a low density material extruded as 100 μm film without stabilizers. All films were washed in alcohol-free chloroform to remove any surface contamination before being used.

Other Techniques

Peroxide contents in natural rubber were determined by iodometric analysis using the method of Carlsson and Wiles [15]. In Nylon the measurement was made by using the oxidation of Fe(II) in hexafluoroisopropanol solution [16]. Electron beam irradiations were carried out at room temperature in a LINAC accelerator at a dose rate of 2.68 kGy min^{-1}.

RESULTS AND DICUSSION

Natural Rubber

Natural rubber is one of the simplest systems for oxyluminescence study. It combines a reasonably high rate of oxidation with detectable chemiluminescence. The polymer is well above its T_g at the temperatures at which it oxidises so that the oxidation can reasonably be modelled as a liquid-phase reaction. Studies of rubbers have been reported by Mendenhall et al. [17] and by Mayo and Davenport [18]. Figure 1 shows the luminescence curve for the steady-state oxidation of a sample of natural rubber. The close parallel with the expected oxidation curve is obvious, suggesting that the intensity of luminescence is proportional to the rate of the oxidation reaction as required by both luminescence mechanisms.

If the sample is heated in a series of stages, it is possible to obtain an Arrhenius plot of the luminescence intensity and this gives an activation energy of the order of 100 kJ mol^{-1}, comparable with values obtained from oxygen absorption and peroxide formation measurements.

A rather more revealing observation is the heating of a rubber sample in nitrogen, after thorough flushing to remove dissolved oxygen. A luminescence peak is produced which can easily be measured at high sensitivity and which decays away to a very low level over a period of minutes to hours, depending on the temperature. Figure 2 shows such a peak on an expanded scale.

The area of this peak represents the total number of photons that are emitted by the sample on heating. For convenience we call this the total luminous intensity (TLI) of the sample. We find that the TLI is directly proportional to the weight of the sample, from which we infer that luminescence is from the whole of the sample rather than a surface layer. The peak has many characteristics suggestive of an association with the peroxide content of the sample. Thus it appears only on the first heating of the sample; if the sample is cooled in nitrogen then reheated there is no further luminescence. Brief exposure to air does not regenerate the peak on reheating but if the sample is allowed to age in air after the experiment then
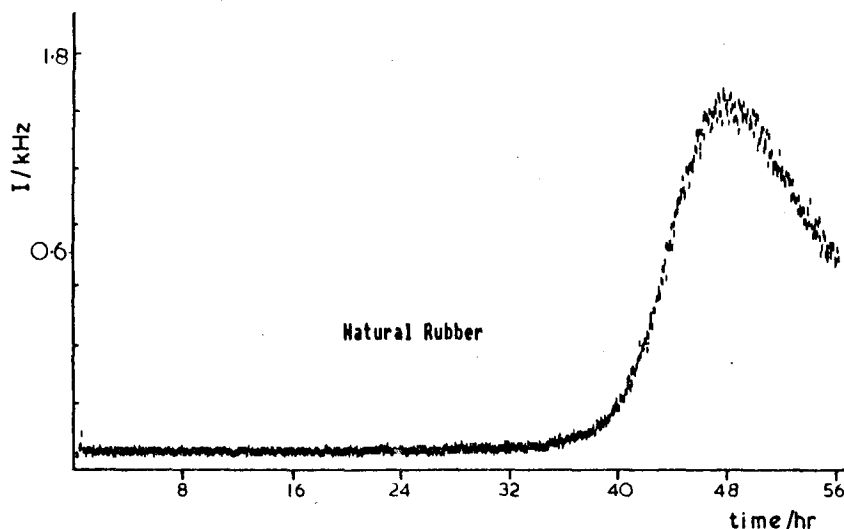

Figure 1. Continuous chemiluminescence from a thin film of natural rubber in oxygen at 80°C.