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USING NITROXIDE DECAY TO STUDY THE PHOTOOXIDATION KINETICS OF AUTOMOTIVE TOPCOAT ENAMELS

J.L. GERLOCK*, D.R. BAUER, and D.F. MIELEWSKI

Research Staff, Ford Motor Company, P.O. Box 2053, Dearborn, MI 48121, USA.

Free radical scavenging by nitroxide dopant is used to quantify the photoinitiation rate of free radicals in acrylic/melamine and polyester/urethane coatings during photolysis under "near ambient" exposure conditions. Photoinitiation rate measurements on weathered coatings reveal that acrylic/melamine coatings photooxidize non-autocatalytically, while polyester/urethane coatings photooxidize autocatalytically. The decomposition of hydroperoxide photolysis products by melamine crosslinker is claimed to account for this difference in photooxidation kinetics.

KEY WORDS: Nitroxide, ESR, acrylic/melamine, polyester/urethane, photooxidation rate, photoinitiation rate, weatherability.

INTRODUCTION

The weatherability performance of automotive clearcoat enamels is determined by the kind of exposure experienced during service, the intrinsic photooxidation resistance of the polymers used, and the ability of additives to inhibit photodegradation. Automotive coatings are amongst the most[1] weather resistant polymers used in the outdoors today. Their photodegradation chemistry is complex and very difficult to simulate in the laboratory. The most reliable weatherability performance information is obtained from actual outdoor exposure tests.[1] While a poor coating may fail after several years of outdoor exposure, a superior coating can retain its initial physical properties for many years. The time required to conduct outdoor exposure tests severely limits the feedback available for both coating development and quality control.

The development of a means to reliably test the weatherability of coatings in the laboratory is a long standing coating industry goal. Numerous artificial (accelerated) weathering tests have been devised.[2] All resort to harsher than natural exposure conditions to accelerate weathering and shorten test time. Unfortunately, harsh exposure can either produce degradation chemistry that does not occur outdoors or distort the relative importance of competing degradation chemistries. As a result, misleading weatherability results, relative to outdoor tests, are not uncommon. Accelerated test results are rarely accepted as sole proof of a new coating system's weatherability performance.

Our research efforts have been aimed at test methods that would not require harsh exposure conditions to shorten test time. Relationships have been sought between coating degradation chemistry and physical degradation. The present work will focus

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*Author to whom inquiries should be addressed.

on the use of electron spin resonance spectrometry (ESR) to quantify the weatherability performance of coatings.

EXPERIMENTAL

Chemicals

Acrylate copolymer compositions are given in ref. 12-a. The chemical compositions of the polyester copolymers studied here are proprietary. Melamine formaldehyde crosslinker Cymel 325 was obtained from American Cyamid. Triisocyanate biuret crosslinker L-2291 was obtained from Mobay. The synthesis of Nitroxide **I** from TEMPAMINE and *n*-octadecyl isocyanate (Aldrich Chemical) is described in ref. 6. TEMPO, TEMPOL, and TEMPAMINE were obtained from Aldrich Chemical. TEMPOL was recrystallized three times from ethanol prior to use.

Equipment

ESR spectra were recorded with a 200-D ESR spectrometer (Bruker) equipped with an Aspect 2000 data system. Coating samples were subjected to FS-40 fluorescent UV-B light in a UV screening device (Atlas) described in ref. 7 and to 320 nm cut off filtered (Schott Glass) xenon arc light in a Ci-35 Weather-ometer (Atlas). Hydroperoxide titrations were performed with a Metrohm automatic titroprocessor.

Procedures

Quantitative analysis of nitroxides in coatings by ESR is described in ref. 6, and more recently ref. 16. Gas-phase doping of coatings with TEMPOL is described in ref. 16. Hydroperoxide titrations were performed on 0.5 g samples of cryogenically ground coating swelled with 10 ml of methylene chloride according to the procedure outlined in ref. 18. The detection limit of the titration procedure is $< 0.5 \times 10^{-6}$ mol/g.

RESULT AND DISCUSSION

The ESR approach to coating weatherability assessment is based on the premise that coatings lose their physical properties primarily as the result of sunlight initiated photooxidation chemistry wherein the oxidation kinetics are not greatly different from that in solution. Thus, applying the steady state approximation to reactive free radical intermediates in the classical hydrocarbon photooxidation Scheme **I**, yields equation **1**[3].

Equation (1) suggests that there should be a direct relationship between photooxidation rate and the square root of the rate at which free radicals are photoinitiated. In theory, photoinitiation rate (PIR) measurements could provide a simple means to rapidly assess the photooxidation resistance of unstabilized coatings.

In practice, the concentration of free radicals in coatings subjected to "sunlight-like" exposure is far too low to measure directly by ESR. ESR signals can be observed when coatings are either exposed to intense ultraviolet (UV) light or photolyzed at low

Init. $A + hr \longrightarrow A^*$
$A^* \longrightarrow 2Y\cdot$

Prop. $Y\cdot + O_2 \longrightarrow \mathrm{YOO}\cdot$
$\mathrm{YOO}\cdot + \mathrm{PH} \longrightarrow \mathrm{YOOH} + \mathrm{P}\cdot$
$\mathrm{P}\cdot + \mathrm{O}_2 \longrightarrow \mathrm{POO}\cdot$
$\mathrm{POO}\cdot + \mathrm{PH} \longrightarrow \mathrm{POOH} + \mathrm{P}\cdot$

Bran. $\mathrm{POOH} + hr \longrightarrow \mathrm{PO}\cdot + \cdot\mathrm{OH}$

Term. $\mathrm{POO}\cdot + \mathrm{POO}\cdot \longrightarrow$ Products (A??)

$$-\frac{d[\mathrm{PH}]}{dt} = \frac{k_p}{k_t^{1/2}}[\mathrm{PH}]\,(\mathrm{PIR})^{1/2} \propto \begin{array}{c}\text{Degradation}\\ \text{Rate}\end{array} \qquad (1)$$

where

$$\mathrm{PIR} = 2ki_1\,[A] + 2k_{i_2}\mathrm{I}\,[\mathrm{POOH}] + \ldots$$

SCHEME 1

temperature, but such conditions are very non-natural. Trial experiments wherein coatings were doped with a persistent nitroxide to scavenge coating based free radicals, reaction (2), suggested that nitroxides could be used to integrate free radical formation over time and eliminate the need for harsh exposure conditions.

$$>\mathrm{NO}\cdot + \mathrm{P}\cdot \longrightarrow\ >\mathrm{NOP} \qquad (2)$$

Reaction **2** is well studied and generally accepted as a key reaction in the inhibition

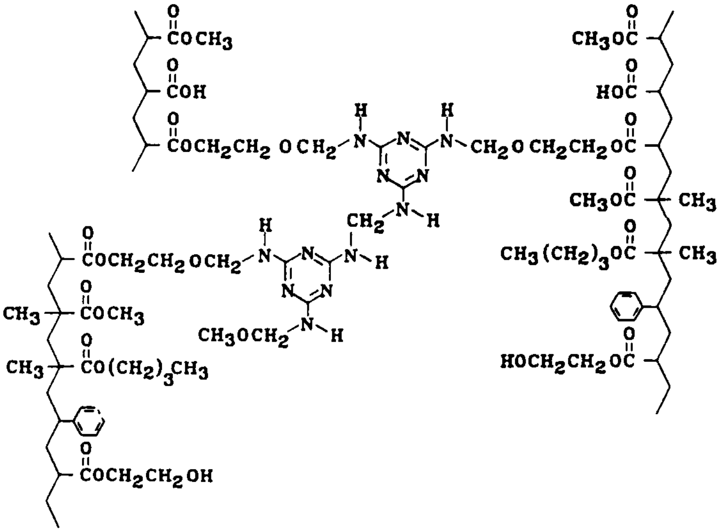
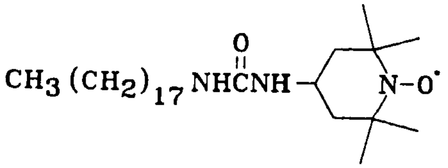


FIGURE 1 Generalized structure of acrylic/melamine coating.

of photooxidation by hindered amine light stabilizers (HALS).[4(a,b)] HALS comprise a family of antioxidants based on the 2,2,6,6-tetramethylpiperidine moiety.[5]

A generalized structure of a highly crosslinked acrylic/melamine coating is shown in Figure 1. When such coatings are doped with non-volatile Nitroxide I, cured at 130°C, and



I

placed in noon, summer sunlight, the concentration of I, as determined by double integration of its ESR signal,[6] decreases measurably in hours, Figure 2. Subsequent experiments under controlled conditions in the laboratory, FS-40 fluorescent UV-B lights at an air temperature of 60°C and a dew point of 25°C (substantially harsher than natural exposure conditions),[7] revealed that nitroxide decay is linear up to 10–15% of the initial nitroxide concentration. The initial rate of decay was found to be dependent on the starting concentration of nitroxide. This is not surprising as excited nitroxides are known to abstract hydrogen atoms,[8] reaction 3.

$$>NO\cdot^{*} + PH \longrightarrow\ >NOH + P\cdot \qquad (3)$$

Free radical formation due to nitroxide photolysis could be separated from that due to coating photolysis by conducting decay measurements at different starting concentrations of nitroxide. Thus a plot of initial decay rate versus starting nitroxide concentration yields a straight line whose intercept can be taken as the PIR of coating based radicals in the absence of nitroxide.[9]

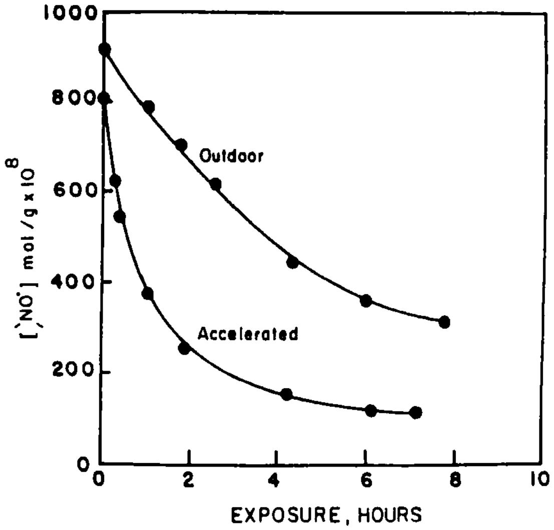


FIGURE 2 Decrease in Nitroxide I concentration in acrylic/melamine coating during outdoor and accelerated UV exposure.

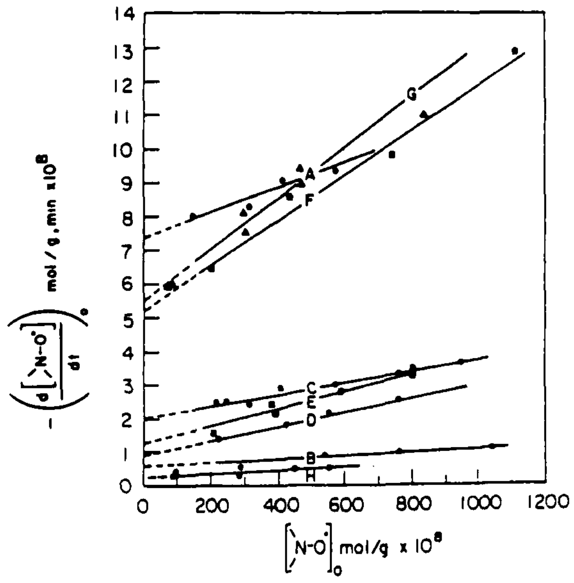


FIGURE 3 Nitroxide I decay during accelerated UV exposure as a function of starting nitroxide concentration for a series of acrylic/melamine coatings.

The results of such measurements are shown in Figure 3 for a series of acrylic/melamine coatings and one oligoester/melamine (H). Large differences in PIR values are observed even though the acrylic/melamine coatings are chemically nearly identical.[10]

In the time since these early experiments, a variety of ancillary experiments have been performed to examine PIR behavior. PIR behavior with light intensity, temperature, humidity, and oxygen concentration;[9] presence of UV-absorber;[11] acrylate copolymer synthesis conditions;[12(a,b)] and the presence of HALS has been examined.[13]

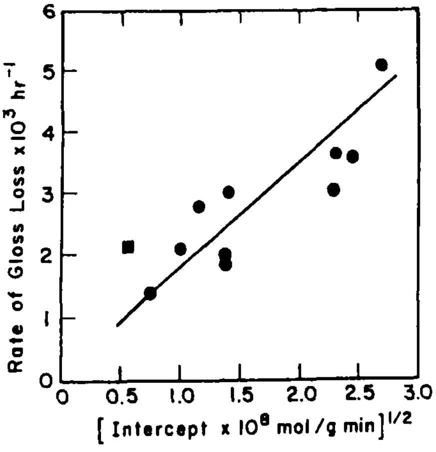


FIGURE 4 Gloss loss rates of TiO_2 pigmented acrylic/melamine coatings versus $PJR^{1/2}$ values of non-pigmented versions. All samples were subjected to the same accelerated UV exposure.

Most interesting, and in agreement with equation (1), a good correlation was found between $(PIR)^{1/2}$ and gloss loss rates, Figure 4. Gloss loss is a standard measure of pigmented coating weatherability.[1] Gloss decreases when chemically degraded resin is lost from the surface of a coating to leave pigment particles exposed to scatter incident light. PIR values were measured for pigment free (clearcoat) coatings, while gloss rates were measured for TiO_2 pigmented samples wherein oxidative degradation is limited to the coating's surface.

The strong correlation observed between PIR value magnitude and gloss loss rate clearly indicated that PIR measurements by "Nitroxide Decay Assay"[9] could be used to rapidly assess the photooxidation resistance of additive free acrylic/melamine coatings in the laboratory. Since completion of that work, laboratory PIR values have been found to accurately rank the outdoor weatherability performance of comparably stabilized acrylic/melamine coatings. The technique is presently being examined by a number of research groups as a coating development tool.

Although the Nitroxide Decay Assay appears to be a useful coating development tool, the technique is very empirical and there are numerous questions as to the generality and limitations of the technique. The present work begins to address these issues.

The most surprising aspect of the Nitroxide Decay Assay is the fact that this brief measurement (hours), performed on freshly prepared acrylic/melamine coatings, can accurately predict the long term (> 6 years) weatherability performance of acrylic/melamine coatings. This suggests that the photooxidation rate of acrylic/melamine coatings must remain relatively constant for many years. Although there is evidence in the literature to support this view,[14(a–c)] photooxidation at a constant rate is at odds with the usual photooxidation kinetics observed for polymers. Polyolefin photooxidation, for example, is characterized by an induction period during which photolabile oxidation products build in concentration to the point that their photolysis begins to contribute to the photoinitiation of free radicals and photooxidation accelerates.[15] Clearly, PIR values determined for freshly prepared polyolefins could not reveal their long term photooxidation behavior.

One means to follow the photooxidation kinetics of acrylic/melamine coatings would be to measure PIR values as a function of weathering time. This measurement is not possible using Nitroxide **I** as dopant. Nitroxide **I** must be added to wet paint prior to cure, and the act of weathering consumes the nitroxide. The measurement becomes possible when a volatile nitroxide is substituted for Nitroxide **I**. Trial experiments with TEMPO, TEMPOL, and TEMPAMINE reveal that these nitroxides readily diffuse into cured acrylic/melamine coatings from the gas phase in the presence of methylene chloride/methanol vapor (10/1 volume ratio) at temperatures as low as 50°C. The diffusion is not uniform in the absence of methanol vapor. Absorbed methanol vapor appears to act as a hydrogen bond transfer agent. Absorbed TEMPO readily desorbs when samples are heated to 60°C in the open air to remove absorbed solvent. In contrast, the desorption of TEMPAMINE and TEMPOL does not become measurable until the temperature is raised above 85°C. It has been suggested that these nitroxides are retained in the coating by hydrogen bonds.[16]

The results of weathering-time resolved PIR measurements using TEMPOL as gas-phase dopant are shown in Figure 5 for four coatings from the series previously studied.[16] Weathering and PIR measurement temperatures were reduced from 60°C to 40°C to minimize TEMPOL volatilization and bring exposure conditions closer to ambient. As can be seen, PIR values decrease during the early stages of exposure to

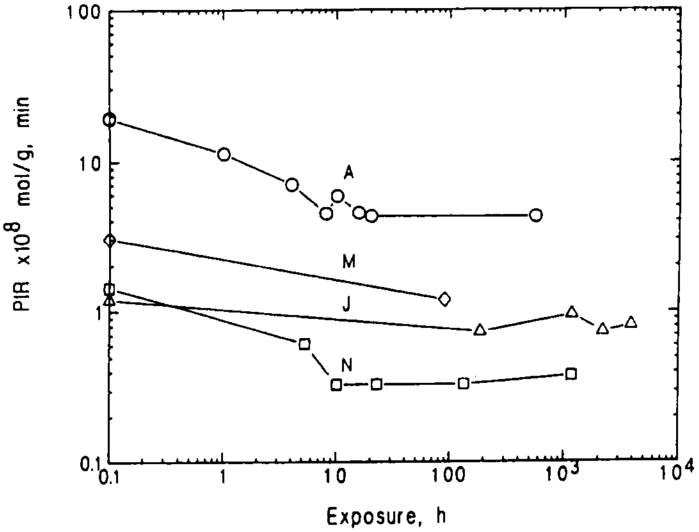


FIGURE 5 Weathering-time resolved PIR value behavior of acrylic/melamine coatings weathered under accelerated UV exposure conditions at 40°C using TEMPOL as gas-phase nitroxide dopant.

values that are sustained for the duration of the experiments. There is no evidence for autocatalytic photooxidation kinetics. The fact that sustained PIR values closely parallel initial (non-weathered coating) PIR values explains how initial values can correctly rank acrylic/melamine coatings according to their photooxidation resistance. Obviously, sustained PIR values provide a more accurate view of absolute photooxidation rates.

It is not clear why there should be a parallel between initial and sustained PIR

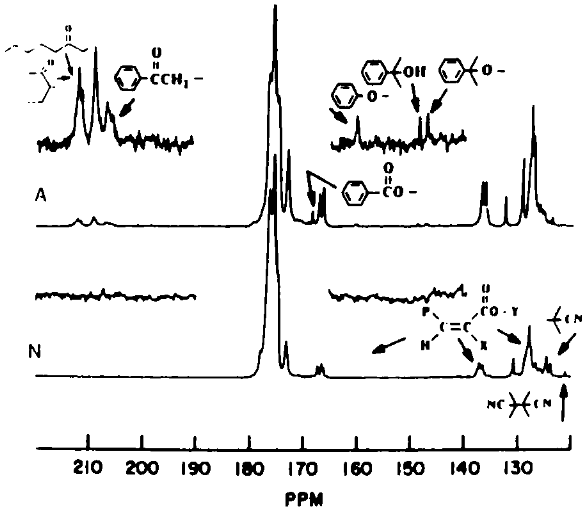


FIGURE 6 Solution ^{13}C NMR spectra of acrylate copolymers used to prepare acrylic/melamine Coatings *A* and *N*.

values. Freshly prepared coatings contain a variety of trace components; solvents, inhibitors, initiators, and unreacted monomers among others, whose photolysis could yield fleetingly high PIR values during the early stages of weathering. The parallel observed in the present series of acrylic/melamine coatings may just be fortuitous. Initial and sustained PIR values do appear to be closely linked to the nature of acrylate copolymer and end-groups. End-group nature is determined during the synthesis of acrylate copolymers by the choice of thermal initiator(s), chain transfer agent(s), and synthesis solvent(s).[12(a–b)] The acrylate copolymer used to prepare coating *A* was synthesized in 2-heptanone with *t*-butylperbenzoate and cumene hydroperoxide as co-initiators. The ^{13}C NMR spectrum of this copolymer reveals the presence of aliphatic and aromatic ketone end-groups, Figure 6. These end-groups are not present in the acrylate copolymer used to prepare low PIR Coating *N*, Figure 6.[17] The latter copolymer was synthesized in xylene with azobisisobutyronitrile (AIBN) as initiator.

The mechanism(s) by which end-groups act to determine sustained PIR values, photooxidation rate and therefore long term weatherability performance, is also not clear. For example, solid state magic angle ^{13}C NMR spectra of Coating *A* recorded as a function of weathering time, Figure 7 and insert, indicate that the concentration of ketone end-groups quickly drops below the detection limit of the spectrometer during the early stages of exposure — a decrease not unlike that observed for initial PIR values.

A series of weathering-time resolved PIR measurements have been carried out on polyester/urethane coatings to test the generality of the nitroxide decay assay coating weatherability prediction technique. The weatherability performance of polyester/urethane coatings is known to be very sensitive to non-natural weather exposure conditions. Harsh exposure accelerated weathering tests invariably suggest that polyester/urethane coatings exhibit poor weatherability, while actual outdoor exposure tests indicate the opposite. The temperature at which samples were weathered and

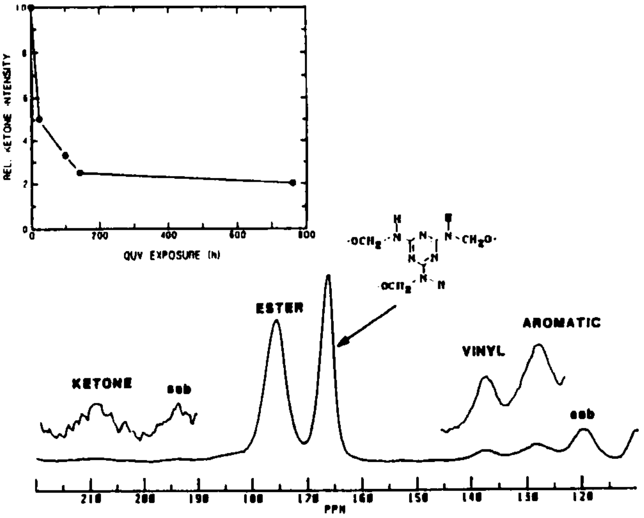


FIGURE 7 Magic angle solid state ^{13}C NMR of Coating *A* with insert showing decrease in aliphatic/aromatic end-groups as a function of accelerated UV exposure time.

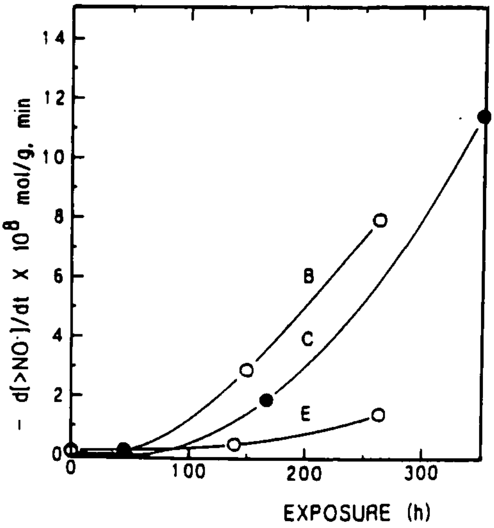


FIGURE 8 "Near ambient exposure" weathering-time resolved PIR value behavior of polyester/urethane coatings.

PIR values measured was reduced in our experiments as a further step toward ambient exposure conditions. In addition, a 320 nm cut off filtered xenon arc light operating at an intensity equivalent to noon, summer, Miami, Fla. sunlight (0.35 W/m^2 at 340 nm) was substituted for the FS-40, UV-B fluorescent light source. The results of these "near ambient exposure" weathering-time resolved PIR measurements are shown in Figure 8[18]. All coating in this series exhibit a low initial PIR value prior to weathering. With weathering, PIR values begin to increase and the photooxidation turns autocatalytic. It is presently thought that the length of the induction period should discern photooxidation resistance differences between polyester/urethane coatings. It is clear that initial PIR values can not be used to make this distinction.

The PIR measurements above clearly reveal a fundamental difference between the photooxidation kinetics of acrylic/melamine and polyester/urethane coatings. Polyester/urethane coatings photooxidize autocatalytically while acrylic/melamine coatings do not. The driving force behind this difference is of immediate interest in that it has direct bearing on the formulation of coatings to maximize photooxidation resistance as well as the selection of additives to inhibit photooxidation.

A series of experiments has been carried out to determine the reason why acrylic/melamine coatings do not photooxidize autocatalytically. The lack of autocatalytic activity suggests that hydroperoxides do not build in concentration during photolysis. Partial results of weathering-time resolved iodometric titrations[19] (KI/thiosulfate) for hydroperoxide are shown in Figure 9, for two coatings; acrylic/melamine Coating *N*, and a urethane crosslinked version of the acrylate copolymer used in Coating *N*. Urethane crosslinks were formed with triisocyanate biuret crosslinker L-2291, the crosslinker used to formulate the polyester/urethane coating above. The hydroperoxide concentration behavior observed for Coating *N* parallels the PIR value behavior observed for this coating with the exception that brief exposure is required to build hydroperoxide concentration to a detectable level before it decreases to a lower level with continued exposure (in progress). Hydroperoxide is not present prior

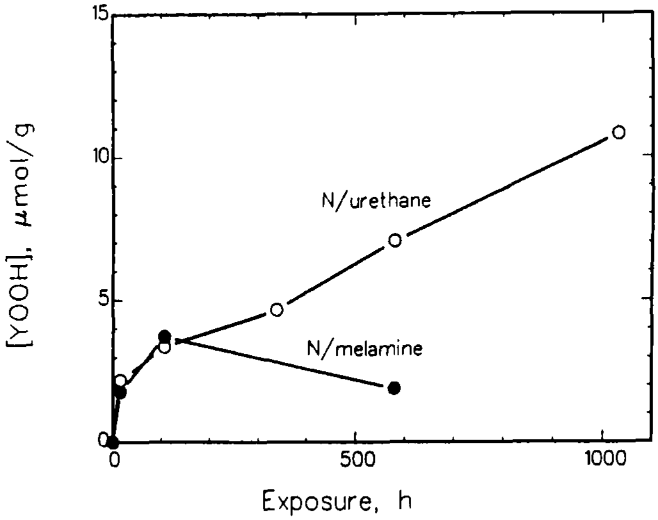


FIGURE 9 Hydroperoxide concentration in acrylic/melamine coating *N*, and a urethane crosslinked version of the acrylate copolymer used to prepare Coating *N*, as a function of UV exposure time.

to weathering. PIR value and hydroperoxide concentration behavior also parallel one another in the case of the urethane crosslinked version of Coating *N*. Aside from the suggestion that hydroperoxide titration could evolve into a "beaker test" of coating weatherability, these results suggest that the melamine crosslinkers may decompose hydroperoxides and preclude autocatalysis. ^{13}C NMR spectra indicate that cumene and *t*-butyl hydroperoxides are rapidly decomposed in d_6-benzene at 60°C by Cymel 325. The methanol urethane of L-2291 triiocyanate does not decompose these hydroperoxides under the same conditions.

CONCLUSIONS

Nitroxide decay PIR measurements provide a ready means to study the photooxidation kinetics of fully crosslinked coatings under "near ambient" exposure conditions in the laboratory. Weathering-time resolved PIR measurements reveal that unstabilized polyester/urethane coatings exhibit autocatalytic photooxidation kinetics while unstabilized acrylic/melamine coatings do not. Hydroperoxide decomposition by melamine crosslinker is suggested to preclude autocatalytic photooxidation in acrylic/melamine coatings.

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