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Photostabilization and photodegradation in organic coatings containing a hindered amine light stabilizer. Part VII. HALS effectiveness in acrylic melamine coatings having different free radical formation rates

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The ability of hindered amine light stabilizer (HALS) bis-(2,2,6,6-tetramethyl-4-piperidinyl) sebacate to reduce the photooxidation rate in two different acrylic melamine polymer coatings has been studied using both infrared and electron spin resonance spectroscopies. These coatings differ primarily in the rate at which free radicals are formed during photolysis. Under controlled photolysis conditions similar to sunlight (near-ambient), the photoinitiation rate (PIR) of free radicals in one coating is some five times higher than that of the other coating, resulting in a photooxidation rate that is some 2·5 times greater than that for the coating with the lower PIR value. When harsh, short wavelength ultraviolet light is used, the PIR values and photooxidation rates of both coatings are higher. The addition of hindered amine (2% by weight) to the coating with the higher PIR value reduces its photooxidation rate by roughly a factor of 2·6 for both exposures. The addition of the hindered amine to the coating with the lower PIR value reduces its photooxidation rate by a factor of 1·9 for the harsh exposure, but does not reduce its photooxidation rate under near-ambient exposure conditions. These results point out the risk of using harsh, accelerated tests to evaluate stabilizer performance and also suggest that there is a limit to HALS inhibition in acrylic melamine coatings.

INTRODUCTION

The development of coatings with improved durability and of more reliable tests for predicting durability requires a better understanding of the chemistry of photodegradation and stabilization. Photooxidation in acrylic melamine coatings, which are widely used as exterior enamels, results in the formation of carbonyl groups, acrylic–melamine cross-link scission, and melamine–melamine cross-link formation.[1,2] One unusual aspect of photooxidation in acrylic melamine coatings is the fact that formaldehyde is given off as a by-product of the cross-link degradation reactions.[1,2] Formaldehyde emission and the rate of photooxidation has been found to increase with increasing humidity.[2,3] Oxidation of formaldehyde to performic acid has been suggested to be important in photooxidation of melamine crosslinked coatings.[2]

One key to the understanding of photooxidation kinetics of stabilizer-free coatings has been the development of the nitroxide decay assay, an ESR technique for measuring free radical formation during photolysis.[4] The assay reveals that the rate of photoinitiation in acrylic melamine coatings drops rapidly on exposure from their initial values to lower, sustained values.[5] The photooxidation rate as measured by carbonyl growth in IR spectra of these coatings is also constant after the initial exposure period, and appears roughly proportional to the square

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root of the sustained photoinitiation rate (PIR),[6] consistent with standard free radical chain oxidation models.[7] The concentration of hydroperoxides measured after the initial weathering period has been found to be roughly proportional to measured PIR values for these coatings.[8]

Both the initial and the sustained PIR values in acrylic melamine coatings are a strong function of the conditions used to synthesize the acrylic copolymer.[9,10] When hydroperoxides and peresters are used as initiators and ketones as solvent, a high concentration of ketonic end groups is incorporated into the acrylic copolymer resulting in high initial and sustained PIR values. When the initiator azobisisobutyronitrile is used in solvents such as xylene, no ketones are observed, and the photoinitiation rate is low. It is not clear, as yet, why high initial PIR values are associated with high sustained PIR values.

Hindered amine light stabilizers (HALS) are typically added to acrylic melamine coatings (as well as other polymers) to reduce the rate of photooxidation. Studies of HALS stabilization in model compounds and in polyolefins has resulted in a number of proposed mechanisms.[11–16] One key mechanism for photostabilization by HALS involves the scavenging of free radicals by HALS and its by-products. The first step in this scheme is the oxidation of HALS to a nitroxide (>NO·). This is followed by reaction of >NO· with a free radical (R·) to form an >NOR compound. The >NOR can regenerate nitroxide via reaction with peroxy radicals, thus completing a stabilizing cycle. A complete understanding of HALS stabilization requires knowledge of the concentrations and reactivities of HALS and all its by-products.

Previous papers in this series have addressed specifically the role of HALS in reducing photooxidation in acrylic melamine coatings.[17–21] Early studies focused on the conversion of one HALS (TIN 770 from Ciba Geigy) to nitroxide[17] and subsequent nitroxide kinetics.[18] The importance of formaldehyde in the HALS stabilization chemistry of acrylic melamine coatings was demonstrated. In later studies, infrared spectroscopic measurements of carbonyl growth in a stabilized and unstabilized acrylic melamine coating were used to quantify the degree of inhibition afforded by the addition of different HALS.[20] This work found that the addition of HALS reduces the photoxidation rate in the particular acrylic melamine studied by factors ranging from 1·2 to 2·6.[20] ESR measurements of nitroxide concentration were used to follow the rate of oxidation of the parent HALS to >NO·.[21] This rate was found to depend on the nature of the substituent group on the piperidine nitrogen. In the acrylic melamine coating studied, oxidation to >NO· was found to be fastest for HALS with >N-H and >N-CH_3 groups, and slower for >N-CH_2CH_2-polymer and >N-CO-CH_3 groups. Interestingly, HALS effectiveness was found to correlate well with the rate of conversion of HALS to >NO·. This suggests that most HALS are not very effective stabilizers until some of the HALS is converted into the >NO·–>NOR stabilizing cycle. For the >N-H functional HALS (TIN 770 from Ciba-Geigy), the inhibition factor increased with increasing HALS concentration up to 1% by weight and then leveled off.

The acrylic melamine used in the above studies had a relatively high photoinitiation rate. It was chosen because it photooxidized rapidly, thereby affording a rapid determination of the HALS effectiveness. In this paper, the previous studies are extended to determine the effectiveness of TIN 770 in reducing photooxidation in an acrylic melamine coating with a very low photoinitiation rate. The results are compared with previous studies and the implications for degradation and stabilization mechanisms are discussed. The utility of accelerated tests in assessing stabilizer effectiveness is also analyzed.

EXPERIMENTAL

Synthesis of acrylic copolymers A and N has been described previously.[22] Copolymer A was synthesized using *t*-butylperbenzoate and cumene hydroperoxide as co-initiators in 2-heptanone. Copolymer A contained 68% by weight butylmethacrylate, 30% hydroxyethylacrylate, and 2% acrylic acid. Copolymer N was synthesized using azobisisobutyronitrile in xylene. Copolymer N contained 58% by weight butylmethacrylate, 40% hydroxyethylacrylate, and 2% acrylic acid. Both copolymers were cross-linked with Cymel 325 (American Cyanamid) using a ratio of 70:30 (by solids weight) polymer to cross-linker to form coatings A-Mel and N-Mel. Bis-(2,2,6,6-tetramethyl-4-piperidinyl) sebacate (TIN 770) was obtained from Ciba Geigy and recrystallized prior to use. A-Mel was used in previous studies and exhibits high initial and sustained PIR values, while N-Mel exhibits low initial and sustained PIR values.

Coatings containing different concentrations of TIN 770 were cast and cured at 130°C for 20 min on NaCl plates (for infrared spectroscopy) and on quartz disks (for electron spin resonance spectroscopy). Samples were weathered using conditions previously described.[6] One exposure, denoted as 'harsh', employs high intensity, short wavelength ultraviolet (UV) light with an air temperature of 60°C and a dew point of 25°C. The other exposure, denoted as 'near-ambient', employs borosilicate filtered xenon arc light with an air temperature of 40°C and a dew point of 25°C. No dark, water spray, or condensing humidity cycles were used.

Infrared spectra were obtained in transmission using a Mattson Sirius 100 FTIR spectrometer as described previously.[6] The extent of photooxidation was followed by comparing IR spectra of weathered and unweathered coatings. Difference spectra were generated as a function of exposure time. The spectra were normalized using the hydrocarbon region. Photooxidation was quantified by integrating the carbonyl region of the difference spectrum.[6]

The concentration of HALS-based nitroxide was measured by ESR using a Bruker ER-220 spectrometer operating at 9·5 GHz. Coating samples cast on 5 mm disks were placed in a specially designed sample holder to insure consistent sample positioning.[5] Concentrations were determined by double integration of first derivative signals relative to primary standards.

RESULTS AND DISCUSSION

Photoinitiation rates have been previously reported for A-Mel and N-Mel under both exposure conditions.[5,6] The sustained PIR values are as follows: A-Mel, harsh exposure, $4{\cdot}5 \times 10^{-8}$ mol/g min; near-ambient, $0{\cdot}18 \times 10^{-8}$ mol/g min; N-Mel, harsh exposure, $0{\cdot}4 \times 10^{-8}$ mol/g min; near-ambient, $0{\cdot}04 \times 10^{-8}$ mol/g min. N-Mel has a significantly lower sustained photoinitiation rate than does A-Mel. In the first few hours of harsh exposure and first few hundred hours of near-ambient exposure, the photoinitiation rates of both coatings are higher than their sustained values. Substantial photooxidation occurs during this initial high-PIR period in A-Mel, particularly under near-ambient exposure.

Infrared spectra of N-Mel before weathering and after near-ambient weathering are shown in Fig. 1. The difference spectrum shows the changes that occur on weathering. As discussed in more detail elsewhere, the increase (positive signal) in the carbonyl region (1800–1500 cm^{-1}) is indicative of oxidation of the acrylic chain and melamine cross-linker.[6] The decrease (negative signal) of intensity at 915 cm^{-1} and the increase in the hydroxy region (3300 cm^{-1}) is indicative of acrylic–melamine cross-link scission. The increase in intensity at 1340 cm^{-1} indicates melamine–melamine cross-link formation. As shown in Fig. 2, the changes that occur on weathering of N-Mel with 2% by weight TIN 770 are identical to those for N-Mel with no HALS. In addition, the observed degradation chemistry of N-Mel is very similar to that previously found for A-Mel with and without HALS. This suggests that the degradation chemistries in these coatings are qualitatively the same, and that the types of degradation chemistry observed in these coatings are not changed by the addition of HALS. Similar results are obtained for the two coatings under harsh exposure conditions.

The extent of chemical oxidation has been quantified by measuring the area under the difference spectrum in the carbonyl region (1800–1500 cm^{-1}). This area is then normalized to the initial absorbance in the hydrocarbon region (thus, correcting for differences in film thickness from sample to sample). Since the addition of HALS does not change the types of degradation chemistry observed, HALS effectiveness in reducing photooxidation can be determined by comparing the rate of increase of carbonyl area in the different coatings with and without HALS. Figure 3 shows plots of the increase in carbonyl area versus near-ambient exposure time for A-Mel and N-Mel with no HALS and with 2% by weight TIN 770. Similar plots are shown in Fig. 4 for the harsh exposure. In addition to reporting data for N-Mel coatings, carbonyl growth in A-Mel coatings has been extended to longer near-ambient exposure times than reported previously.[20] In all cases, after the initial exposure period, the plots of carbonyl growth versus exposure time can be fitted to straight lines whose slope is proportional to the rate of photoxidation. The relative photooxidation rates are reported in Table 1. The following comparisons can be made: for a given copolymer and exposure condition, the effectiveness of

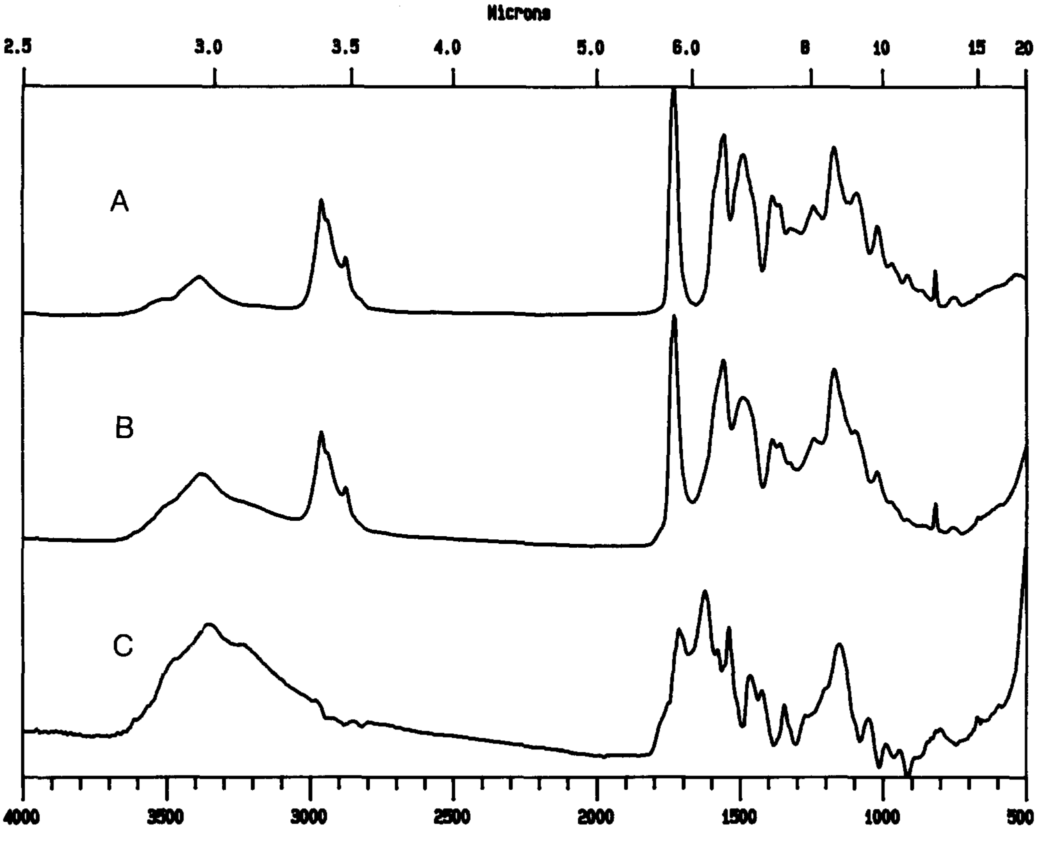

Fig. 1. Infrared spectra of N-Mel. Spectrum A is from an unweathered coating, while spectrum B is from a coating weathered 6312 h under near-ambient exposure. Spectrum C is the difference spectrum.

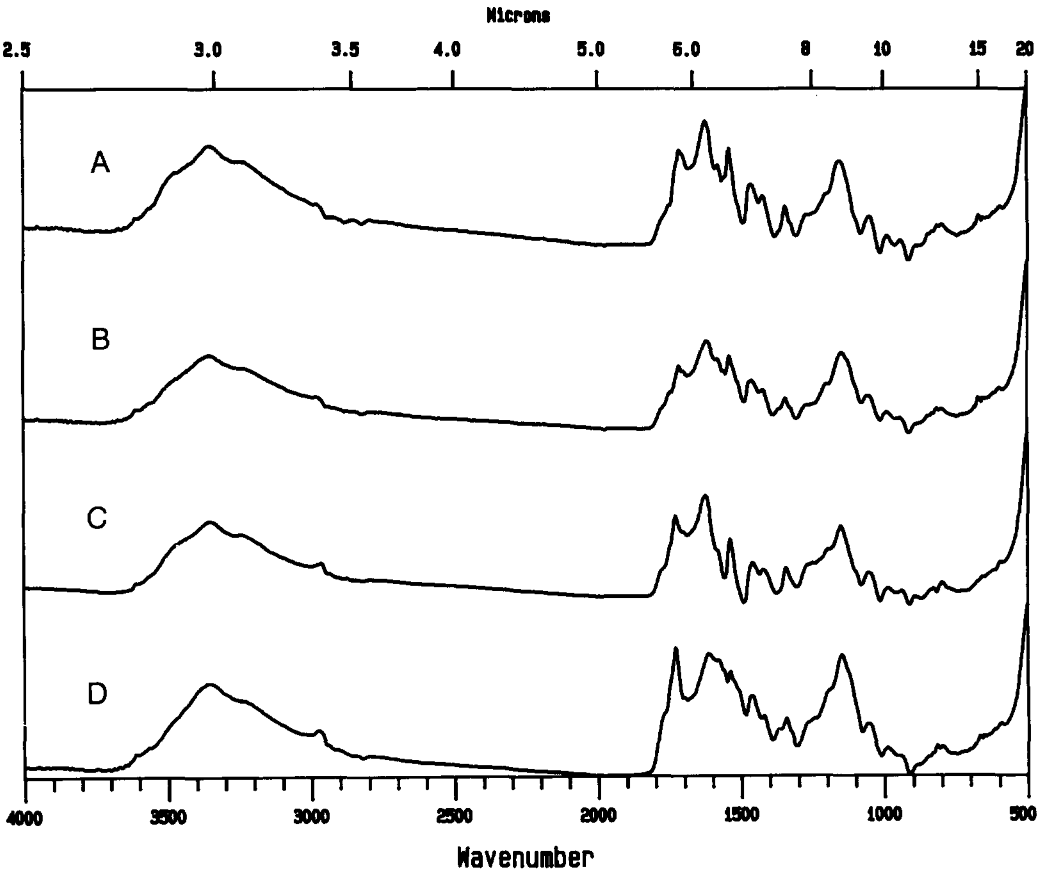

Fig. 2. Infrared difference spectra. Spectrum A is the difference spectrum for N-Mel before and after 6312 h of near-ambient exposure. Spectrum B is a similar spectrum for N-Mel with 2% TIN 770. Spectrum C is the difference spectrum for A-Mel before and after 3680 h of near-ambient exposure. Spectrum D is a similar spectrum for A-Mel with 2% TIN 770 except that the exposure time is 6312 h.

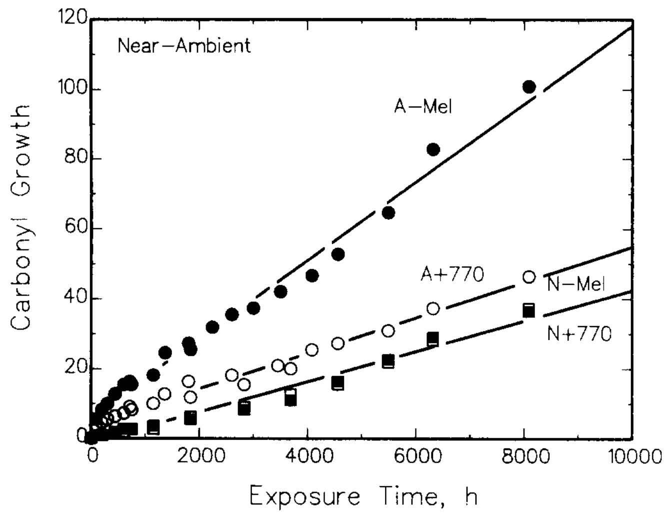

Fig. 3. Carbonyl growth versus near-ambient exposure time for A-Mel and N-Mel with and without 2% by weight TIN 770.

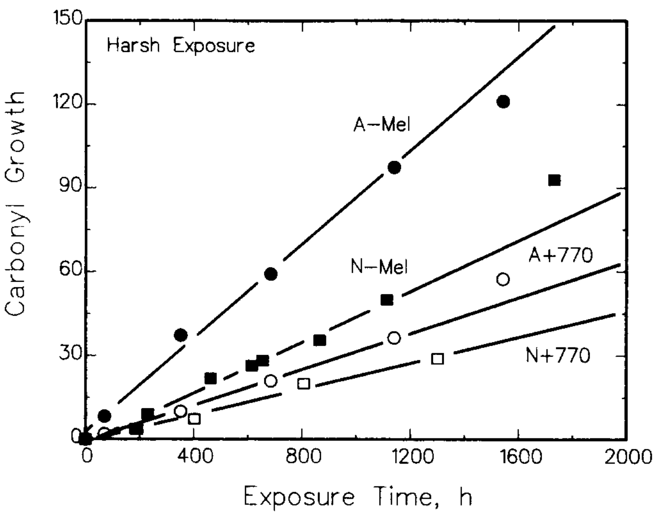

Fig. 4. Carbonyl growth versus harsh exposure time for A-Mel and N-Mel with and without 2% by weight TIN 770.

HALS inhibition can be evaluated; for a given stabilizer and exposure condition, the role of copolymer (A versus N) can be determined; and for a given coating, the acceleration factor of the harsh exposure relative to the near-ambient exposure can be measured. These comparisons are reported in Tables 1–3.

Table 1. Photooxidation rates for acrylic melamine coatings

Copolymer	% TIN 770	Harsh	Near-ambient	Acceleration factor
A	0	0·088 0	0·011 5	7·7
A	2	0·033 0	0·004 7	7·0
N	0	0·043 0	0·004 3	10·0
N	2	0·022 5	0·004 3	5·2

The photooxidation rate is expressed as the increase in carbonyl area divided by the exposure time. Since the carbonyl area is in arbitrary units, the photooxidation rates are relative.

Table 2. TIN 770 inhibition factors (2% by weight)

Copolymer	Exposure	Inhibition factor
A	Harsh	2·7
A	Near-ambient	2·5
N	Harsh	1·9
N	Near-ambient	1·0

The inhibition factors reported in Table 2 for A-Mel agree well with those previously reported for this coating.[20] The long-term inhibition factor for near-ambient exposure in A-Mel does not change with extended exposure time (5000–8000 h). The inhibition factor for the harsh exposure is nearly identical to that of the near-ambient exposure. By contrast, the addition of 2% TIN 770 to N-Mel reduces the photooxidation rate in the harsh exposure by a factor of 1·9, but does not reduce the photooxidation rate at all in the near-ambient exposure. This result points out the danger of using accelerated tests to evaluate stabilizer performance. The harsh exposure suggests that the addition of TIN 770 results in a substantial improvement in durability. This is not realized in the more realistic near-ambient exposure. The addition of other HALS such as TIN 079L to coating N-Mel has also been found not to inhibit near-ambient photooxidation.

As reported in Table 3, the rate of carbonyl growth in unstabilized N-Mel is lower than that for unstabilized A-Mel by a factor of 2 for the harsh exposure and 2·7 for the near-ambient exposure. The predicted ratios based on the square root of the PIR values are 3·3 for the harsh exposure and 2·2 for the near-ambient exposure. The addition of TIN 770 reduces the difference in photooxidation between A-Mel and N-Mel, particularly for the near-ambient exposure. In fact, the photooxidation rate for stabilized A-Mel under this exposure is nearly identical to the rate for N-Mel.

Table 3. Photooxidation rates of A versus N

% TIN 770	Exposure	Ratio of rates in A to N
0	Harsh	2·0
0	Near-ambient	2·7
2	Harsh	1·5
2	Near-ambient	1·1

Harsh accelerated tests are often used to evaluate and/or optimize new stabilizer packages for coatings. The above results suggest that data from such tests can be very misleading. The problem with accelerated tests is that the acceleration factor (see Table 1) depends on the coating as well as the test. Simms has also reported variations in acceleration factor with different coating technologies for a particular accelerated test.[23] The data in Table 1 suggest that the acceleration factor can vary by as much as a factor of 2 for as small a formulation change as the addition of a light stabilizer or a change in copolymer. Such variations in acceleration factor cannot be predicted *a priori*. Thus, the utility of accelerated tests in optimizing coating systems or verifying the effects of formulation changes on durability is highly questionable.

In all cases studied to date, inhibition of photooxidation in acrylic melamine coatings by TIN 770 is incomplete. In A-Mel, the inhibition factor increases with increasing TIN 770 concentration up to 1% and then levels off. The photooxidation rate in A-Mel stabilized with ≥1% TIN 770 is similar to that for N-Mel with or without stabilizer. This suggests that there may be a limit to which HALS can reduce the photooxidation rate in acrylic melamine coatings. Stabilization models based on free radical scavenging reactions of HALS and its byproducts suggests that at high enough concentrations HALS can almost completely inhibit free radical photooxidation.[19] Complete inhibition is typically observed in polyolefins during a lengthy induction period.[11] In the paragraphs that follow, possible reasons for the failure of HALS to completely inhibit photooxidation in acrylic melamine coatings are suggested.

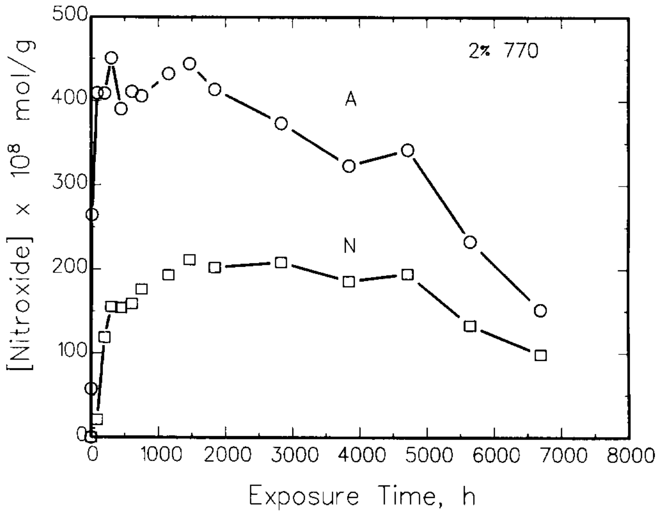

Fig. 5. Nitroxide concentration versus near-ambient exposure time for A-Mel and N-Mel with 2% by weight TIN 770.

It has been previously shown in these coatings that HALS are effective only after some of the HALS has been converted into the >NO· – >NOR cycle. One possibility for the lack of effectiveness of TIN 770 in N-Mel is that the rate of conversion of TIN 770 to >NO· is slow in this coating. Measurements of >NO· concentration as a function of near-ambient exposure time are shown in Fig. 5 for A-Mel and N-Mel with 2% TIN 770. The >NO· concentration reflects the concentration in the >NO· – >NOR cycle. The rate of initial net formation of nitroxide is much slower for N-Mel than coating A-Mel consistent with the lower initial photooxidation rate in N-Mel. After this initial period (~500 h of exposure), the nitroxide concentration in the two coatings parallel one another and both coatings reach their maximum nitroxide concentration after roughly 2000 h of exposure. This is consistent with the data of Fig. 3 which show that the oxidation rate in the two coatings with TIN 770 are identical after 500 h exposure. The level of nitroxide in N-Mel with 2% TIN 770 is roughly the same as that for A-Mel with 1% TIN 770. A level of 1% TIN 770 is sufficient to reduce photooxidation in A-Mel. Thus, the rate of conversion of TIN 770 to nitroxide cannot account for the observed lack of effectiveness in N-Mel.

Another possibility is that a portion of the photodegradation chemistry occurring in acrylic melamine coatings cannot be controlled by HALS. From the infrared spectra in Figs 1 and 2, this chemistry must produce the same degradation products as the free radical photooxidation chemistry which is reduced by the addition of HALS. It should be noted that treatment of these coatings with peracid does generate products similar to that produced by photooxidation. It is possible that the formaldehyde-based peracid chemistry which results from melamine cross-link scission is responsible for the failure of HALS to completely inhibit photodegradation.

It is also possible that limits to HALS effectiveness are 'built-in' to the different stabilizing reactions. For example, Klemchuk and Gande have demonstrated that ketone groups are produced during the reaction of >NOR species with peroxy radicals.[14] Ketones are chromophores for photooxidation in these systems.[10] Production of chromophores during stabilization may lead to a limiting rate of photooxidation. Decomposition of >NOR back to nitroxide and a free radical could also limit overall HALS effectiveness. Carlsson *et al.* have shown that some >NOR species are thermally unstable.[11] If >NOR decomposes before reacting with a peroxy radical then the stabilizing cycle would be broken. The stability of these compounds depends on the nature of the 'R' group. Attempts to identify the nature and reactivity of these species in these coatings are under way.

CONCLUSION

HALS effectiveness in acrylic melamine coatings has been found to be a function of both the intrinsic photooxidation rate of the coating and of the exposure condition used. The use of harsh exposure conditions commonly used in accelerated tests can provide misleading results regarding stabilizer performance. Under 'outdoor-like' exposure conditions, it is found that HALS are less effective in reducing photooxidation in coatings with low unstabilized photooxidation rates than they are for coatings with high photooxidation rates. There appears to be a limit to which HALS can reduce photooxidation in acrylic melamine coatings.

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