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Photo-Stabilisation and Photo-Degradation in Organic Coatings Containing A Hindered Amine Light Stabiliser. Part I—ESR Measurements of Nitroxide Concentration

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ABSTRACT

Quantitative measurements of the variation in nitroxide free radical concentration on exposure to ultraviolet (uv) light are reported for a melamine crosslinked acrylic copolymer film doped with a hindered amine light stabiliser (bis (2,2,6,6-tetramethyl-4-piperidinyl) sebacate) as a function of hindered amine concentration, light intensity and humidity. The concentration of nitroxide is found to rise to a maximum and then slowly decrease. The following parameters can be derived from the nitroxide data: the net rate of formation of nitroxide during the early stages of exposure, the maximum nitroxide concentration, the time to maximum and the net decay rate at long exposure times. The observed variations in these parameters with exposure conditions are discussed. It is found that the humidity of the exposure greatly influences the degradation and stabilisation chemistry of acrylic–melamine coatings.

INTRODUCTION

Hindered amine light stabilisers (HALS) based on 2,2,6,6-tetramethylpiperidines are widely used to reduce ultraviolet (uv) light induced oxidative degradation of polymers subject to outdoor exposure. The chemistry of stabilisation by HALS additives has been reviewed recently by several authors.[1–6] Despite the wide use of HALS in a variety of

Polymer Degradation and Stability 0141-3910/86/$03·50

polymers, including plastics, elastomers and coatings, most mechanistic studies of HALS chemistry have been limited to model compounds,[7-16] polypropylene[17-29] and, to a lesser extent, polyethylene and other polymers.[18,30-32] From these studies it has been generally agreed that HALS are neither uv absorbers nor excited state quenchers. Although HALS themselves are rather weak antioxidants, they and their byproducts are thought to interfere with the propagation of free radical oxidation through reactions denoted in Fig. 1.[1-6] HALS compounds are oxidised to hindered amine nitroxides by photo-induced oxidants in the polymer. Nitroxides react with free radicals (e.g. alkyl, acyl) in the polymer to form aminoethers. The aminoethers can react with photo-induced oxidants in the polymer to regenerate nitroxide. In addition to the mechanism in Fig. 1, other mechanisms of stabilisation have been suggested for HALS. It has been suggested, for example, that HALS and their byproducts associate with, and decompose, hydroperoxides.[25,28] The kinetics of HALS stabilisation is further complicated by the fact that hindered amine nitroxides are photo-labile.[33,34] Excited state nitroxides can abstract hydrogen atoms, producing a free radical and hydroxyl amine. Nitroxide photo-chemistry has been generally ignored in the treatment of HALS stabilisation.

The effectiveness of HALS in polymers depends on the relative rates of reactions involving the formation and consumption of nitroxide and on the rates of photo-oxidation reactions. Thus, it can be expected that the degree of stabilisation imparted by a HALS additive will depend on the structure of the HALS, the degradation chemistry of the polymer and the exposure conditions employed. With the introduction of high solids and basecoat/clearcoat coatings, the use of HALS in organic coatings exposed outdoors has increased dramatically.[35] There have been relatively few published studies of stabilisation chemistry of HALS in polymeric

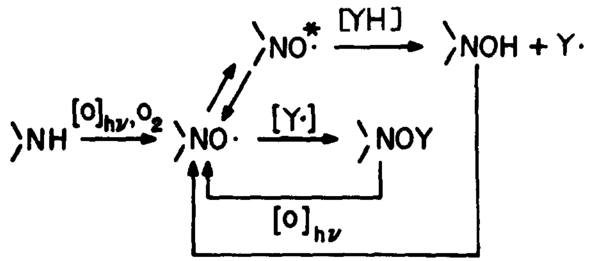
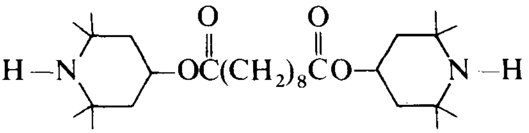


Fig. 1. Hindered amine light stabiliser chemistry.

coatings. Gerlock *et al.*[36,37] have measured the concentration of nitroxide in acrylic/melamine coatings doped with a hindered amine as a function of exposure time. The observed variation in nitroxide level with time was a strong function of the acrylic copolymer used, though no single parameter was found which correlated with the overall photo-oxidation rate in these coatings. It was also found that increased humidity during exposure increased the net formation rate of nitroxide in the early stages of exposure.[36] It was suggested that this was due to formaldehyde which is produced as a byproduct of hydrolysis of acrylic-melamine crosslinks. Formaldehyde can be readily oxidised to peracid which can rapidly convert hindered amine to nitroxide.

With the lack of mechanistic studies of HALS-containing coatings, the selection of specific HALS compounds for specific coatings has been largely empirical. It is impossible to predict, on mechanistic grounds, the effectiveness of HALS in providing stability to organic coatings. The goal of the present work is to improve the understanding of the stabilisation chemistry of HALS in polymeric coatings. The ideal approach to such a study would be to monitor the concentration of HALS and all of its byproducts as a function of exposure time and other variables. Although such measurements have been made for polypropylene,[27] it has not proved feasible to measure all the components formed during photolysis of crosslinked polymeric coatings. The present study has been confined to measurements of the concentration of HALS additive and nitroxide as a function of exposure time, exposure conditions and coating crosslinking chemistry. The study is divided into three parts. In the first paper, ESR is used to monitor the concentration of nitroxide free radical in an acrylic/melamine coating doped with a particular hindered amine, bis (2,2,6,6-tetramethyl-4-piperidinyl) sebacate, (HALS I) as a function of exposure time and exposure conditions:



A number of parameters describing the variation in concentration with exposure time are determined and the changes in the values of these parameters with changes in exposure conditions are discussed. For comparison, the concentration of nitroxide in an acrylic/urethane coating doped with HALS I has also been measured. Comparisons of the behavior in the melamine and urethane coatings can isolate the rôle of formaldehyde in stabilisation and degradation chemistry since the hydrolysis reaction which forms formaldehyde precursors in the melamine coating does not exist in the urethane coating. Comparison of the melamine and urethane coatings is continued in the second paper[38] in this series which reports gas chromatographic measurements of the concentration of HALS I as a function of exposure time and exposure conditions. Two previously unsuspected reactions involving HALS I are also reported. In the final paper[39] in this series the data of the first two papers are interpreted using a kinetic scheme based on conventional free radical oxidation. The rate constants for the different reactions in Fig. 1 are determined and their variation with coating composition and exposure conditions discussed.

EXPERIMENTAL

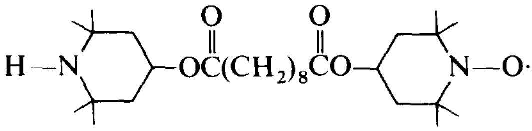
The acrylic copolymer used in this study is the same as that used in coating G in previous work.[40] It was prepared by conventional free radical polymerisation using 30 % by weight hydroxyethylacrylate, 25 % styrene, 23 % butylmethacrylate, 20 % 2-ethylhexylacrylate and 2 % acrylic acid. The polymer had a number average molecular weight of 2300. Two crosslinkers were used in this study. The first was a partially alkylated melamine formaldehyde resin (Cymel 325 from American Cyanamid). It was mixed with the copolymer in the ratio 70:30 copolymer:crosslinker. The second was an aliphatic triisocyanate (biuret of hexamethylene diisocyanate) (L2291A from Mobay). It was mixed with the copolymer using a ratio of NCO:OH of 1:1. The two coatings will be referred to as acrylic/melamine (or melamine) and acrylic/urethane (or urethane). It is important to note that the coatings differ only in crosslink chemistry and that the acrylic copolymer is identical in both coatings. HALS I was obtained from Ciba-Geigy Corp. and recrystallised before use. No nitroxide was detected in the recrystallised sample. Coatings containing HALS I were cast on precision cut quartz slides (37 mm × 10 mm × 1 mm) and cured in an air circulating oven for 20 min at 130 °C. Coating film thicknesses were around 100 microns.

Nitroxide concentrations before and after exposure were measured using an IBM-Brucker ESR spectrometer equipped with an Aspect 2000 data system using procedures previously described in detail.[41] Nitroxide concentrations were reproducible to better than ± 5 % except at the lowest nitroxide concentrations measured.

Samples were exposed in a modified Atlas UV-2 weathering chamber previously described.[42] The chamber was modified so that the dew point and the air temperature could be controlled simultaneously. The air temperature was maintained at 60 °C while the dew point was varied between −40 and 50 °C. The light source consisted of two FS-20 fluorescent tubes. The uv light intensity was varied with neutral density filters and ranged from 0·2 to 1·5 mW/cm^2. At the highest light intensity studied, the photo-initiation rate of free radicals in the coatings (as determined by a previously described nitroxide doping assay[42–44] was 12×10^{-8} moles/g, min. Photo-initiation rates have been shown to be proportional to light intensity and independent of humidity.[44] Photo-initiation rates of the melamine and urethane coatings were essentially identical at constant light intensity.[44] Since the photo-initiation rate is an important parameter in the photo-oxidation scheme of the third paper[39] in this series, light intensities are reported in terms of photo-initiation rates. Samples were removed periodically from the weathering chamber and the nitroxide concentration determined. Samples were then replaced in the chamber. The amount of time the samples were left unexposed was found not to affect the measured nitroxide concentration.

RESULTS AND DISCUSSION

A small, but non-zero, level of nitroxide is observed in both coatings after cure but before exposure in the weathering chamber. The level is proportional to the initial HALS I dopant. At a dopant level of 2% by weight, the initial concentration of nitroxide was 12×10^{-8} mole/g in the acrylic/melamine coating and 6×10^{-8} mole/g in the acrylic/urethane coating. On exposure in the weathering chamber, the level of nitroxide increases to a maximum, then slowly decreases. Although the source of the nitroxide signal is the hindered amine, the exact structure(s) of the nitroxide molecule(s) detected cannot be determined from the spectrum. The room temperature nitroxide spectrum is that of a highly immobilised nitroxide (Fig. 2).[45] Initially, it seems likely that the nitroxide has the following structure:



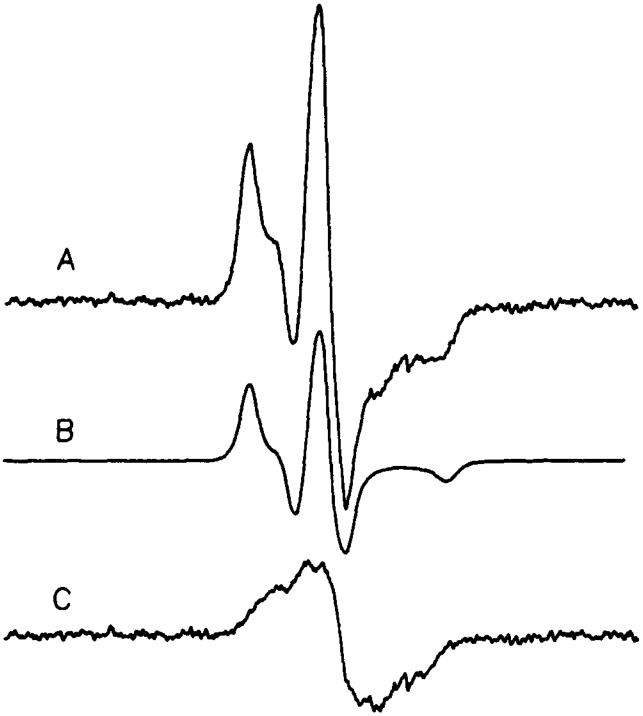
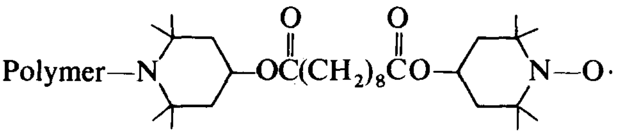
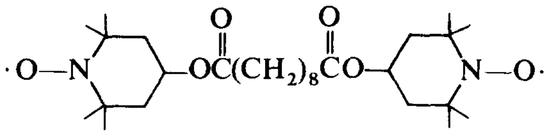


Fig. 2. Hindered amine based nitroxide ESR signal in the acrylic/melamine coating. Signal A is at a very early stage of exposure (1·5 h). Signal B is after extensive exposure (100 h). The difference between signals A and B is the signal from the secondary radical observed in the early stages of exposure (signal C). The vertical scales are arbitrary.

As the exposure proceeds, some of the nitroxide may have this structure:[46]



Dinitroxide species are also possible:



It is impossible to differentiate these species in the observed nitroxide signal.

During the first few hours of exposure at the higher light intensities, a second radical can be observed. The signal is broad and centered near the center of the nitroxide signal (Fig. 2). This signal can be detected in coatings not containing HALS and can be reasonably assigned to the formation of peroxy radicals. The concentration of this secondary radical never exceeds 20×10^{-8} mole/g. As the nitroxide concentration builds up the contribution from this secondary radical decreases. After about 10 hours' exposure it is impossible to detect its signal in the presence of the nitroxide signal.

Plots of nitroxide concentration versus time are shown for the acrylic/melamine coating as a function of light intensity (Fig. 3), humidity (Fig. 4) and HALS I dopant level (Figs 5 and 6). As yet it is not possible to write simple expressions which can describe the observed time dependence of the nitroxide concentration during uv exposure. However, it is possible to measure a number of parameters from the nitroxide

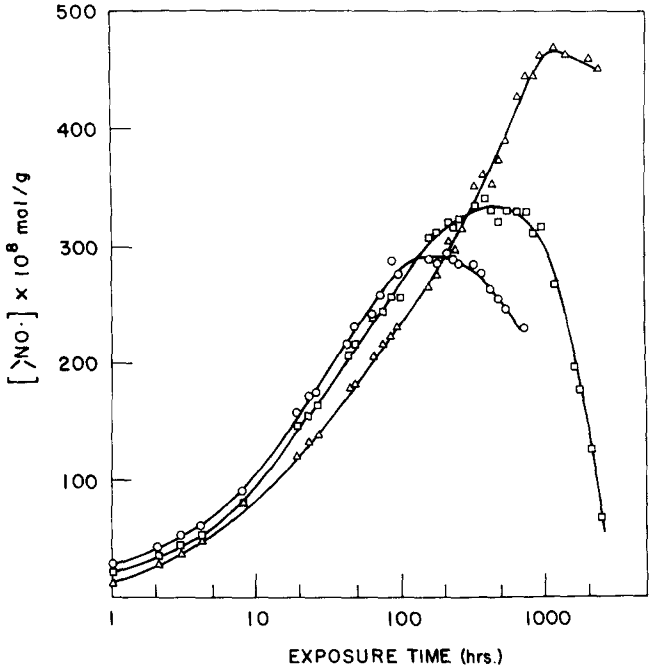


Fig. 3. Nitroxide level versus exposure time for the acrylic/melamine coating exposed at a dew point of 25 °C. The photo-initiation rates of free radicals were 12×10^{-8} moles/g, min (○), 7×10^{-8} moles/g, min (□) and $1{\cdot}4 \times 10^{-8}$ moles/g, min (△). The level of HALS I was 2 % by weight.

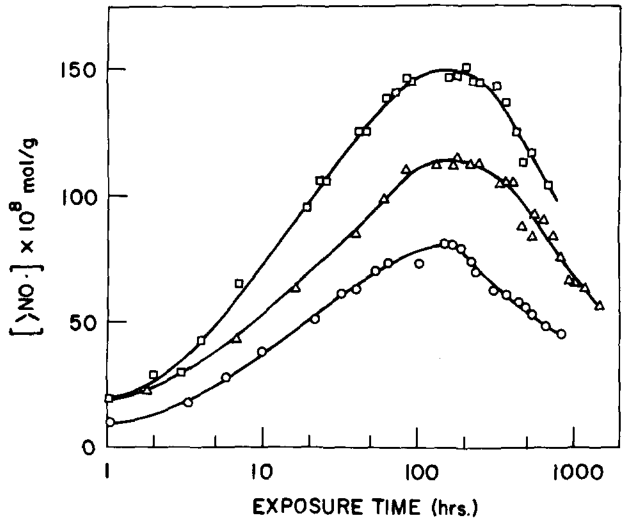


Fig. 4. Nitroxide level versus exposure time for the acrylic/melamine coating exposed with a photo-initiation rate of 12×10^{-8} moles/g, min. The level of HALS I was 1 % by weight. The dew points were −40 °C (○), 25 °C (□) and 50 °C (△).

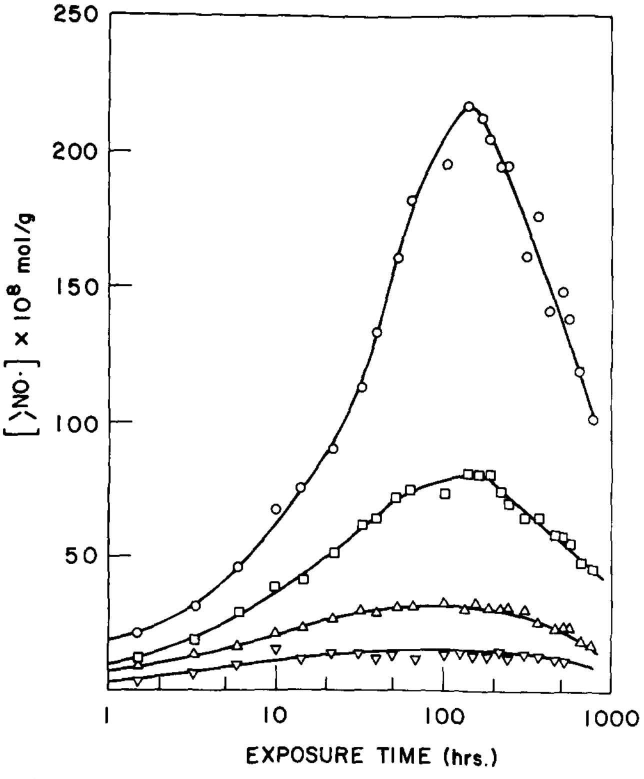


Fig. 5. Nitroxide level versus exposure time for the acrylic/melamine coating exposed at a dew point of −40 °C and with a photo-initiation rate of 12×10^{-8}moles/g, min. The levels of HALS I dopant were 2 % (○), 1 % (□), 0·5 % (△) and 0·25 % (▽) by weight.

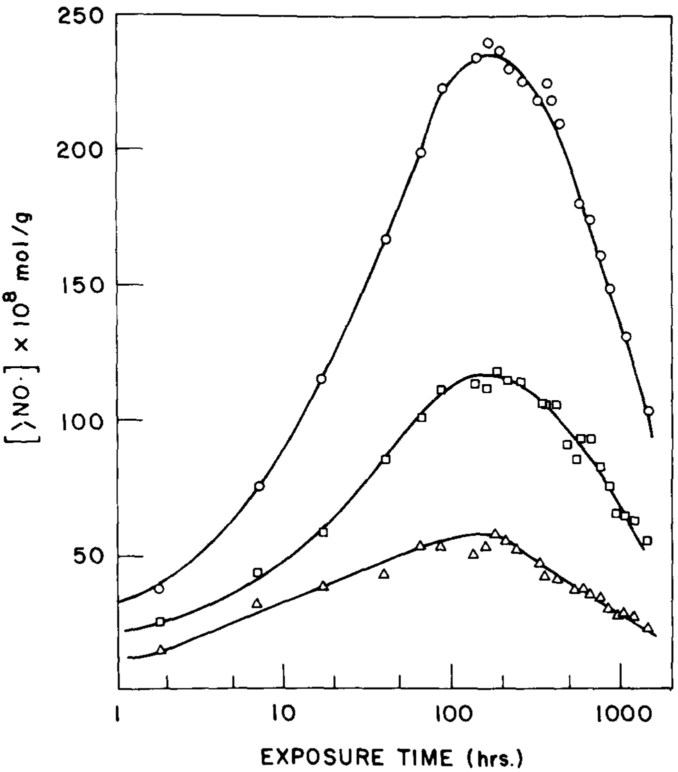


Fig. 6. Nitroxide level versus exposure time for the acrylic/melamine coating exposed at a dew point of 50 °C and with a photo-initiation rate of 12×10^{-8} moles/g, min. The levels of HALS I dopant were 2% (○), 1% (□) and 0·5% (△) by weight.

data, including the net formation rate of nitroxide during the early stages of exposure ($d[>NO\cdot]/dt_i$), the maximum nitroxide concentration ($>NO\cdot_{max}$), the time to reach maximum (t_{max}) and the rate of decay of nitroxide at long exposure times, k_{decay}. In the sections that follow the dependence of these parameters on exposure conditions are discussed.

Net nitroxide formation rate

As shown in Fig. 7, in the early stages of exposure of the acrylic/melamine coating, nitroxide concentration increases linearly with time up to about 25% of $>NO\cdot_{max}$. From the slopes of the lines, $d[>NO\cdot]/dt_i$ can be determined to $\pm 10 - 15\%$. The initial increase in nitroxide in the acrylic/urethane coating is also linear with time (Fig. 8). The variation of

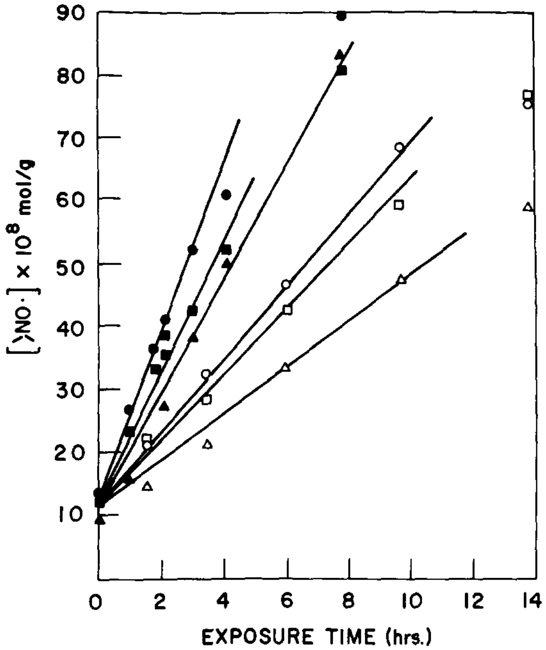


Fig. 7. Nitroxide level versus exposure time during the early stages of exposure for the acrylic/melamine coating doped with 2% by weight HALS I. The open symbols are for exposure at a dew point of −40 °C while the closed symbols are for exposures at dew points of 25 °C and 50 °C. The photo-initiation rates were 12×10^{-8} moles/g, min (○, ●), 7×10^{-8} moles/g, min (□, ■) and $1{\cdot}4 \times 10^{-8}$ moles/g, min (△, ▲).

nitroxide concentration with time always reflects the competition between nitroxide formation and consumption (Fig. 1). Thus, the observed value of $d[\rangle NO\cdot]/dt_i$ is always a net formation rate, rather than an absolute formation rate. Values of the net nitroxide formation rates are given in Table 1 for both coatings. Net nitroxide formation rates in the acrylic/melamine coating more than double on increasing the dew point from −40 °C to 25 °C but are independent of humidity at dew points above 25 °C. Net nitroxide formation rates increase with increasing concentration of HALS I, although they are not exactly proportional to HALS I concentration. The observed light intensity dependence was unexpected. It was originally thought that the net formation rate of nitroxide might reflect the rate of photo-oxidation.[36] It has been observed that the photo-oxidation rate is proportional to the square root

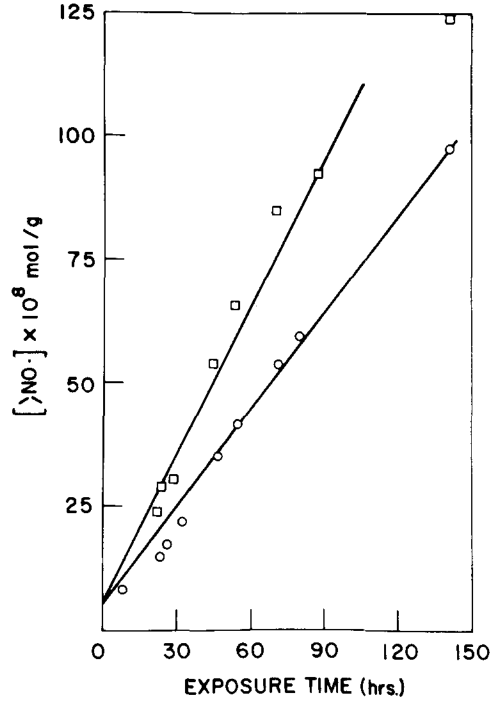


Fig. 8. Nitroxide level versus exposure time during the early stages of exposure for the acrylic/urethane coating doped with 2 % by weight HALS I. The photo-initiation rate was 12×10^{-8} moles/g, min and the dew points were −40 °C (○) and 25 °C (□).

of the light intensity.[37] As can be seen from Table 1, the net nitroxide formation rate does not depend in any straightforward way on light intensity. In some cases the net formation rate even decreases as the light intensity increases. In the third paper of this series,[39] a kinetic scheme which can account for this behavior is presented.

The net formation rates in the acrylic/urethane coating are much smaller than those in the acrylic/melamine coating under the same conditions. Also, the dependence on humidity is smaller in the acrylic/urethane coating. As was suggested earlier,[36] formaldehyde chemistry can account for the observed variation in net nitroxide formation rate. It has been shown that acrylic/melamine crosslinks are subject to hydrolysis, yielding melamine methylol groups, reaction (1):[47]

$$\text{—NCH}_2\text{OR} \xrightarrow{H_2O} \text{—NCH}_2\text{OH} + \text{ROH} \qquad (1)$$

TABLE 1
Early Stage Net Nitroxide Formation Rates × 10^8 mole/g, min

Dew point: [HALS I]	*$W_i \times 10^8$ mole/g, min*	*−40 °C*	*25°, 50 °C (average)*
	Acrylic/melamine Coating		
2	12·0	0·095	0·240
2	7·0	0·092	0·182
2	1·4	0·068	0·140
1	12·0	0·047	0·147
1	7·0	0·067	0·142
1	1·4	0·067	0·100
0·5	12·0	0·023	0·105
0·5	7·0	0·028	0·128
0·5	1·4	0·024	0·092
	Acrylic/urethane Coating		
2	12·0	0·012	0·016

(HALS I in % by weight).

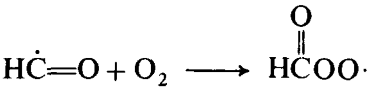
Ultraviolet light is found to accelerate reaction (1).[40] The methylol groups have been found to self condense, yielding formaldehyde, reaction (2):[40,47]

$$2\text{—NCH}_2\text{OH} \longrightarrow \text{—NCH}_2\text{N—} + \text{H}_2\text{C}{=}\text{O} + \text{H}_2\text{O} \tag{2}$$

Formaldehyde contains easily abstractable hydrogens, reaction (3):

$$\text{H}_2\text{C}{=}\text{O} + \text{Y}\cdot \text{ or } \text{YOO}\cdot \longrightarrow \text{H}\dot{\text{C}}{=}\text{O} \tag{3}$$

The H$\dot{\text{C}}$=O radical can be oxidised to a peracid precursor, reaction (4):



$$\text{H}\dot{\text{C}}{=}\text{O} + \text{O}_2 \longrightarrow \text{H}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{OO}\cdot \tag{4}$$

Peracids are known to rapidly oxidise hindered amines to nitroxide.[15,48] This would tend to increase the net formation rate of nitroxide. The difference between the formation rate in the acrylic/urethane and the acrylic/melamine at −40 °C dew point may be due simply to deformylation of unreacted methylol groups which would occur slowly even in the absence of humidity. The observation that the net formation rate of nitroxide is constant at dew points above 25 °C may be due to the fact that peracid production could be limited by the concentration of radicals, as well as by the concentration of formaldehyde. If the formaldehyde release rate is large compared with the rate of generation of radicals then not all the formaldehyde will be converted to peracid and the peracid level (and the nitroxide formation rate) should approach a plateau value. Calculations based on measured hydrolysis rates suggest that the release rate of formaldehyde into the coating is comparable with the photo-initiation rate at a dew point of 25 °C in the acrylic/melamine coating. Other effects of formaldehyde on the stabilisation chemistry have been observed and will be discussed in the second paper in this series.[38]

The measured nitroxide formation rates are much smaller than the photo-initiation rates as measured by the nitroxide doping technique. This suggests that either relatively few of the radicals produced convert amine to nitroxide or that subsequent reactions rapidly convert nitroxide to amino ethers as soon as they are made. Measurements presented in the second paper in this series[38] of the rate of consumption of HALS I during exposure of these coatings demonstrate that, in fact, both explanations are true.

Maximum nitroxide concentration

Values for the maximum nitroxide concentration reached during exposure of the acrylic/melamine coating are presented in Table 2. It can be seen that the maximum nitroxide concentration increases with decreasing light intensity. The maximum nitroxide concentration is a function of humidity, increasing as the humidity increases from −40 °C dew point to 25 °C dew point, then decreasing slightly as the dew point is increased to 50 °C. Values for $>\mathrm{NO}\cdot_{\mathrm{max}}$ can be fitted to the following empirical expression:

$$>\mathrm{NO}\cdot_{\mathrm{max}} = \frac{A[\text{HALS I}](1 + B[\text{HALS I}])}{1 + D\sqrt{W_i}} \qquad (1)$$

where [HALS I] is the initial hindered amine concentration, W_i is the photo-initiation rate (proportional to light intensity) and A, B and D are constants that depend only on the humidity of the exposure. Values of $>\mathrm{NO}\cdot_{\mathrm{max}}$ derived from eqn (1) together with values of A, B and D, are given in Table 2. Note that the values of B and D are similar at dew points of 25 °C and 50 °C, again suggesting that, to a large extent, the nitroxide kinetics are only weak functions of humidity above a dew point of 25 °C.

TABLE 2
Maximum Nitroxide Concentration × 10^8 mole/g

Dew point:	W_i	*−40°C*		*25°C*		*50°C*	
[HALS I]		*Expt*	*Eqn (1)*	*Expt*	*Eqn (1)*	*Expt*	*Eqn (1)*
2	12·0	218	218	292	303	237	238
2	7·0	258	249	337	340	267	268
2	1·4	340	341	450	442	345	348
1	12·0	81	77	150	159	113	110
1	7·0	97	88	172	179	125	124
1	1·4	125	120	225	233	165	161
0·5	12·0	30	30	88	82	54	53
0·5	7·0	36	35	101	92	62	59
0·5	1·4	48	48	116	119	77	77
0·25	12·0	13	13				
0·25	7·0	16	15				
0·25	1·4	23	21				

[HALS I] % by weight.
$W_i \times 10^8$ mole/g, min.

A (x 10^8) =	100	325	195
B =	0·72	−0·05	0·09
D =	0·36	0·27	0·27

The implications of the value of $>\mathrm{NO}\cdot_{\max}$ to the stabilisation kinetics of HALS I are discussed in more detail in the final paper in this series.[39]

Time to maximum nitroxide concentration

Although the maximum nitroxide concentration can be measured to within ±5%, it is difficult to determine accurately the time to maximum. This is because the nitroxide concentration is a very slowly changing function of time near the maximum. As shown in Figs 3–6, the nitroxide concentration remains within 75% of its maximum value for a large fraction of the total exposure time. Thus, even though the values of the nitroxide concentration are very reproducible, $t_{\max}$ can only be determined to about ±25%. Values of $t_{\max}$ are presented in Table 3. Values of $t_{\max}$ decrease slightly with decreasing HALS I concentration. As expected, $t_{\max}$ increases with decreasing light intensity. At a dew point of

TABLE 3
Time to Nitroxide Maximum (h)

Dew point:	W_i	*−40°C*	*25°C*	*50°C*
[HALS I]				
2	12·0	160	200	180
2	7·0	260	450	330
2	1·4	650	1 200	1 200
1	12·0	150	180	180
1	7·0	220	300	250
1	1·4	500	900	900
0·5	12·0	120	160	180
0·5	7·0	200	200	250
0·5	1·4	350	600	850

[HALS I] % by weight.
$W_i \times 10^8$ mole/g, min.

−40 °C, t_{max} varies as the inverse square root of the light intensity while at dew points of 25 °C and 50 °C, t_{max} is roughly inversely proportional to the light intensity. Values of t_{max} are not sensitive to humidity above a dew point of 25 °C.

Long time nitroxide decay rate

After reaching the maximum concentration, the nitroxide levels in the HALS I doped coatings slowly begin to decrease. As can be seen from Fig. 9, the loss of nitroxide can be given by the following equation:

$$\mathrm{d}[{>}\mathrm{NO}\cdot]/\mathrm{d}t = -k_{\mathrm{decay}}\ {>}\mathrm{NO}\cdot_{\mathrm{max}}(t - t')$$

where t' is slightly greater than t_{max}. The above expression gives a somewhat better fit to the data at large nitroxide losses than does the equation used previously[37] which fits well down to a nitroxide concentration of ${>}\mathrm{NO}\cdot_{\mathrm{max}}/2$. Values of k_{decay} are given in Table 4. Values for the nitroxide loss rate constant are proportional to light intensity and are somewhat greater at −40 °C than at 25 °C or 50 °C dew point. The values of k_{decay} are independent of HALS I concentration within experimental error. It has previously been found[37] that k_{decay} is not strongly dependent on coating composition for a series of acrylic/melamine coatings. This, together with the dependence on light intensity,

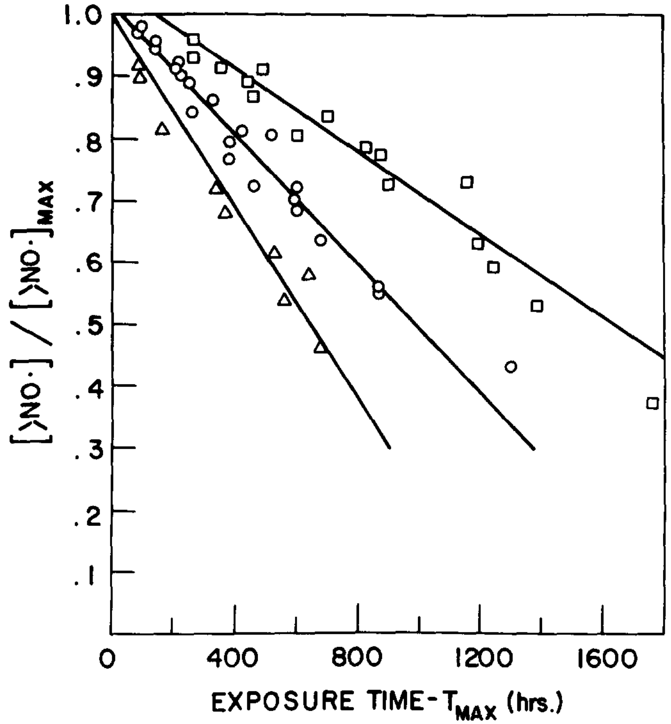


Fig. 9. Loss of nitroxide level at long exposure times in the acrylic/melamine coating doped with 2% by weight HALS I for a photo-initiation rate of 12 × 10^{-8} moles/g, min and a dew point of 25 °C (○), for a photo-initiation rate of 7 × 10^{-8} moles/g, min and a dew point of 25 °C (□) and for a photo-initiation rate of 1·4 × 10^{-8}moles/g, min and a dew point of −40 °C (△).

suggests that the mechanism for loss of stabiliser from the coating may be a direct photo-chemical process. Understanding of this mechanism is important since it essentially determines the lifetime of the stabiliser in the coating.

Implications to accelerated tests

The variation of the nitroxide kinetics in hindered amine stabilised coatings has direct implications concerning the value of accelerated test results on stabilised coatings. Considering the complex variation of the nitroxide kinetics with light intensity and humidity, it is hard to imagine an accelerated test which could reliably and uniformly accelerate the

TABLE 4
$k_{decay} \times 10^6 \text{ min}^{-1}$

Dew point $W_i \times 10^8$ *mole/g, min*	$-40\,°C$	*25°, 50°C* *(average)*
12	13·0	8·8
7	—	5·5

reactions involving HALS additives and their byproducts. In particular, if the acceleration involves light intensities that are much higher than ambient, the accelerated test may discriminate against stabilised coatings since the rate of depletion of stabiliser increases with light intensity whilst, in general, the photo-oxidation rate only increases with the square root of the light intensity. Thus, accelerated tests may deplete the stabiliser at an earlier stage in the degradation than would occur during natural exposure.

CONCLUSION

The concentration of nitroxide has been determined by ESR in an acrylic/melamine coating doped with a hindered amine light stabiliser as a function of exposure conditions and exposure time. The nitroxide concentration is found to increase to a maximum, then slowly decay. The details of the kinetics are a complex function of the light intensity and the humidity of the exposure. There is a qualitative difference between exposure under dry conditions and under humid conditions. The net rate of formation of nitroxide at the early stages of exposure is much more rapid under humid, than under dry, conditions. The maximum nitroxide concentration is greater, and the rate of decay of nitroxide at long times is slower, under humid than under dry exposure conditions. The maximum nitroxide concentration decreases with increasing light intensity and the long time nitroxide decay rate is proportional to light intensity. Surprisingly, the initial net nitroxide formation rate is not a strong function of light intensity over the range studied. The initial net nitroxide formation rate is some 10–100 times smaller than the photo-initiation rate of free radicals. The variation in nitroxide concentration reflects the balance of formation and consumption of nitroxide. In order to gain a better understanding of the magnitude of the flux of the stabilisation chemistry, the rate of consumption of hindered amine has been measured. The results are reported in the next paper in this series.[38] The values of the rate of consumption of hindered amine are compared with the net rate of formation of nitroxide in the final paper of this series.[39]

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