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# Rates of photooxidation induced crosslinking and chain scission in thermoset polymer coatings
## II. Effect of hindered amine light stabilizer and ultraviolet light absorber additives

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**Abstract**

The chemical stress relaxation behavior of two acrylic/melamine clearcoats has been investigated to determine the effect of hindered amine light stabilizers (HALS) and ultraviolet light absorbers (UVA) on the rates of photooxidation induced crosslink/chain scission and crosslink formation. The addition of a HALS to one of the clearcoats, Mel′-A, slows the rate of crosslink/chain scission and in high enough concentrations stops the formation of crosslinks. In the other clearcoat, Mel′-N, the addition of small amounts of either HALS or UVA slows the rate of photooxidation. The overall changes in crosslink density are the same for Mel′-A containing small amounts of HALS and for Mel′-A containing moderate amounts of both HALS and UVA, indicating that the same changes in crosslink density can be achieved by different degradation pathways. These findings indicate that small changes in clearcoat stabilization packages can have dramatic effects on long-term weathering performance of acrylic/melamine coatings.

*Keywords:* Photooxidation; Crosslink density; Relaxation; HALS

## 1. Introduction

The automotive coatings industry is increasingly turning to sophisticated measurement techniques to anticipate the long-term weathering performance of coating systems. These sophisticated methods are being used in conjunction with traditional tests that measure properties such as hardness, gloss, and DOI. While simple tests can be useful, by themselves they are not sufficient to anticipate the long-term weathering performance of modern basecoat/clearcoat paint systems. This is because basecoat/clearcoat systems weather in a fundamentally different manner than monocoat paint systems. Monocoat paints weather gradually, and their rate of weathering is proportional to their rate of gloss loss, which is easily measured. Basecoat/clearcoat systems weather in a more complex manner and can potentially be visually appealing until catastrophic failures occur. Thus, simply measuring visual metrics need not adequately anticipate potential basecoat/clearcoat durability issues.

Many of the recently developed methods for evaluating the weathering performance of coatings have been focused on the chemical changes that take place during the photooxidation of acrylic/melamine and acrylic/urethane clearcoats [1–10]. This work has been reviewed by Bauer [11]. In these materials the main mechanism of weathering induced degradation is photooxidation [7]. Fourier transform infrared spectroscopy (FT–IR) can be used to detect the formation of carbonyl containing photooxidation products such as aldehydes, ketones, and carboxylic acids [1]. For some coatings, specific infrared bands can be associated with the disappearance of certain crosslinks during the weathering process. The rate of disappearance of these crosslinks was shown to be first-order in crosslink concentration [5]. Electron spin resonance (ESR) has been used to measure the rate of formation of free radicals in polymers [2]. High free

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radical formation rates have been linked to high photooxidation rates. Additionally, the concentration of hydroperoxide in clearcoats has been measured using iodimetric titration [3]. Hydroperoxides are involved in the photooxidation process to the extent that their concentration behavior can provide a means to measure photooxidation rate. Finally, a limited amount of nuclear magnetic resonance (NMR) work has been done to assess the changes in crosslink structure that occur as the result of weathering [12–14].

Most of the above methods suffer from the same drawback: the weathering performance of clearcoats from different chemical families cannot be compared because the types of chemical changes that occur are highly dependent on the original coating chemistry. This has recently been addressed by following both film loss (as measured by disappearance of the CH infrared band) [15] and the growth of the –OH, –NH region of the IR spectrum [16,17] — as these are thought to be more generic measures of photooxidation in clearcoats. Most of the chemical techniques are also limited to the analysis of single isolated coating layers, while potential failures typically involve entire paint systems. This, however, is also beginning to change. A recent report by Gerlock et al. suggests that time-of-flight secondary ion mass spectrometry (TOF–SIMS) can be used to assess the weathering resistance of multilayer systems weathered in an $^{18}O_2$ enriched environment [18]. The use of micro-spectroscopic techniques (both IR and UV) also appears promising for examining multilayer systems [19,20].

Additives can play a key role in determining the long-term weathering performance of clearcoats. Both hindered amine light stabilizers (HALS) and ultraviolet light absorbers (UVAs) are typically added to clearcoats to improve their weathering performance and to screen the underlying coating layers from harmful radiation. HALS inhibit photooxidation by scavenging oxidation propagating free radicals, thereby reducing the number potentially reactive species in the coating. UVAs work by absorbing ultraviolet light that could otherwise initiate photooxidation. Alone or in combination the two additives can dramatically reduce the rate of photooxidation, as measured by changes in the chemical composition of the coatings [15].

Weathering tests based on chemical composition change rates provide no information about the physical repercussions of the chemical changes. Therefore, these tests can make no comment on the physical tolerance of clearcoats to the chemical composition changes they undergo, leading to possibly erroneous conclusions regarding their weathering performance. Weathering-induced chemical changes that effect crosslink density are more likely to effect physical performance than those that occur on side groups. Two extremes in chemical change behavior are easily envisioned. In one extreme, the chemical composition changes that take place in a clearcoat may lead to roughly equal rates of crosslink formation and crosslink/chain scission, leading to limited physical property changes. At the other extreme, a different clearcoat may undergo a slower overall rate of photooxidation, but the specific photooxidation chemistry may give rise to primarily crosslink formation, with dramatic physical property consequences. These changes in crosslink density as a function of weathering have been successfully monitored by dynamic mechanical analysis (DMA). Hill and co-workers have shown that modulus measurements in the rubbery plateau region can yield quantitative values for the crosslink density [21–25]. The net effect of weathering on coatings can be either an increase or decrease in crosslink density, depending on the formulation of the coating and the weathering conditions. In addition, the effect of additives has been examined in both composite basecoat/clearcoat films and in isolated clearcoats. For acrylic/melamine coatings the crosslink density tends to increase as weathering progresses in coatings formulated without HALS and decrease in coatings formulated with HALS. In acrylic/urethane coatings the crosslink density tends to decrease as weathering progresses and the addition of HALS generally slows down the rate of crosslink density decrease. However, these results were obtained on films artificially weathered for only 500 h or less.

We have shown recently that the technique of chemical stress relaxation can be used to independently evaluate the rates of crosslink formation and crosslink/chain scission during photooxidation [26]. The relative rates of these processes can change during weathering and can be influenced by subtle changes in the polymer structure. In this paper, we employ chemical stress relaxation to study the effects of HALS on the rates of crosslink formation and crosslink/chain scission in a two acrylic/melamine clearcoats. The results of these experiments will be compared to the known effects of HALS on the rate of chemical composition change in these same polymers.

## 2. Experimental

### 2.1. Materials

Clearcoat films were prepared from two different acrylate copolymers crosslinked with the same melamine resin. The copolymers are referred to as acrylate A and acrylate N. Acrylates A and N were synthesized with the same ratio of butylmethacrylate (58%), hydroxyethylacrylate (40%) and acrylic acid (2%) monomers. Acrylate copolymer A was synthesized in 2-heptanone using t-butylperbenzoate and cumene hydroperoxide (CHP) as co-initiators, while acrylate copolymer N was synthesized in xylene using azobisisobutyronitrile (AIBN) as the sole initiator. Synthesis in 2-heptanone with CHP results in the formation of photoreactive aliphatic and aromatic ketone end-groups, whose photolysis has been claimed to increase photooxidation rate [27,28]. Acrylate copolymers A and N were crosslinked with the same fully alkoxylated mixed methyl/butyl melamine crosslinker (Resimene 755, Monsanto Co.) in a 70:30 acrylate copolymer:melamine crosslinker weight ratio. 0.3% p-tolunesulfonic acid (PTSA) was used as a catalyst. Cured films are referred to as Mel′-A and Mel′-N to denote the different copolymers from which they are formulated. This notation differs from past reports where the clearcoats were referred to as Mel-A and Mel-N [note lack of prime (′)]. This differentiation is due to formulation differences between the clearcoats in this work and past research. Mel′-A and Mel′-N were formulated with a fully alkoxylated melamine crosslinker while Mel-A and Mel-N were formulated with a partially alkoxylated (Cymel 325, Cytec Co.) melamine. In addition, the Mel-A and Mel-N contained no acid catalyst (PTSA).

Tinuvin 123 HALS and Tinuvin 900 UVA (both Ciba Specialty Chemicals) were added in various concentrations to the clearcoats. Films were cast on thin aluminum shim stock using Bird applicators. All samples were cured in a forced air oven at 120°C for 30 min. Free films were made by bending the aluminum substrates until the coating popped off the substrate. Small dogbone specimens were cut from each film using a small die.

### 2.2. Chemical stress relaxation

The chemical stress relaxation technique used, has been described elsewhere [26]. In brief, free films of the clearcoat are tested inside a modified QUV weathering chamber held at a constant temperature and humidity with constant UV radiation from FS-340 bulbs (see Fig. 1). The clearcoat film is placed in a small load frame inside the QUV and a small extension is applied to the clearcoat. The extension under which the clearcoat is held remains constant. The load required to maintain that extension is monitored throughout the experiment. From this experiment the rate of crosslink/chain scission can be determined. This is termed a continuous relaxation experiment. An intermittent relaxation experiment can be used to measure the net changes in crosslink density of a clearcoat. In this experiment, the clearcoat is not constantly extended during exposure. At certain intervals the clearcoat is extended and the load is monitored for a brief period of time, and then the extension is returned to zero. Changes in the load at the end of the short relaxation experiment as a function of weathering can be related to the net changes in crosslink density in an analogous manner as can be done using dynamic mechanical analysis. The advantage of chemical stress relaxation measurements is its ability to measure changes in network parameters after much greater extents of weathering than can DMA. Schematics of the extension and load history for both types of experiments are shown in Figs. 2 and 3.

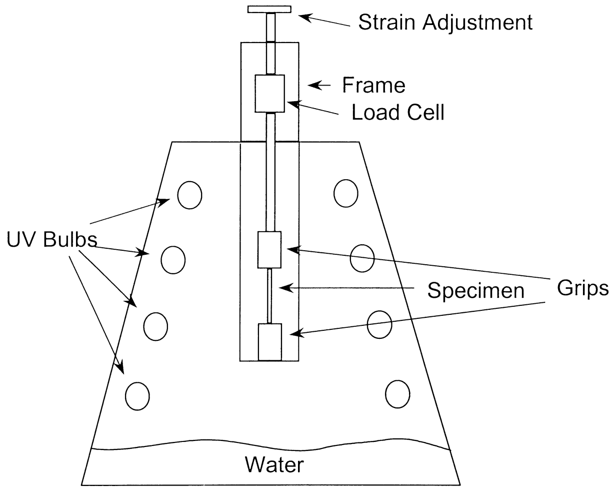

Fig. 1. Schematic of apparatus used to measure chemical stress relaxation behavior of clearcoat films.

All of the experiments described in this paper were conducted at 80°C air temperature and a dew point of 25°C. The clearcoat films were approximately 50 μm thick and 4 mm wide with a gauge section 25.4 mm long. The samples in the continuous relaxation experiments were exposed for up to 2000 h. The samples in the

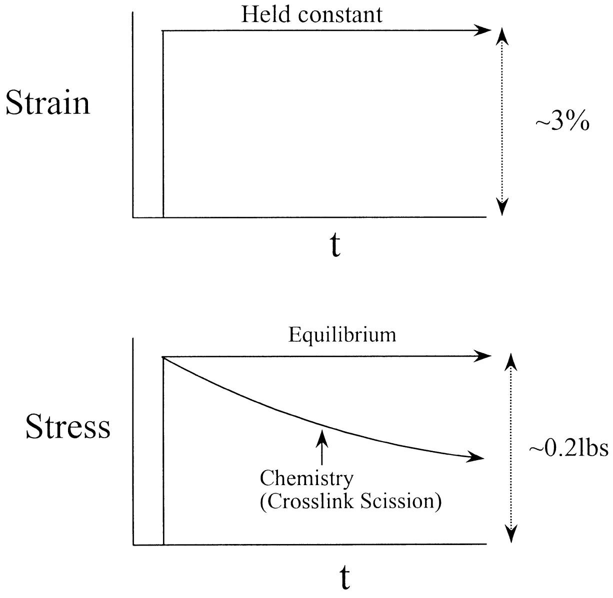

Fig. 2. Hypothetical load and strain history for clearcoat during a continuous stress relaxation experiment. Horizontal line represents behavior of a material undergoing no chemical changes at its equilibrium load. Curved line represents the results of crosslink/chain scission.

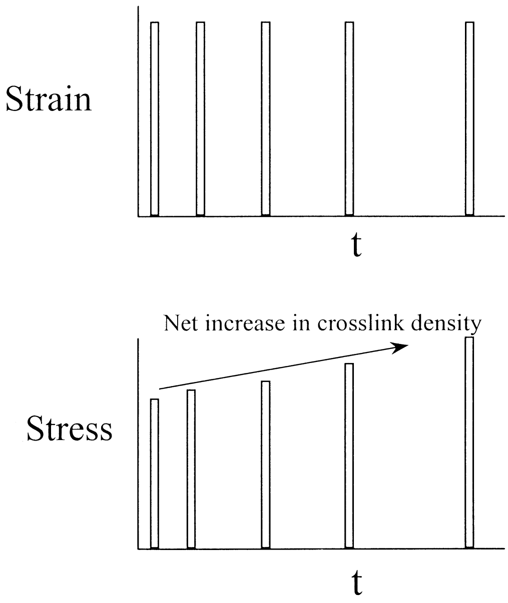

Fig. 3. Hypothetical load and strain history for a clearcoat during an intermittent stress relaxation experiment. Increasing loads for each strain pulse indicate increasing crosslink density.

intermittent relaxation experiments were also exposed for up to 2000 h with a 2.5 min load cycle applied every few days. The strains used were 2.9% for each specimen.

### 2.3. Fourier transform infrared spectroscopy

Fourier transform infrared (FT–IR) spectra were obtained using a Mattson FTIR 5000 at 4 $cm^{-1}$ resolution. Clearcoats were coated and cured on 1 cm diameter silicon discs and placed in the same QUV as the relaxation specimens. The discs were periodically removed and the spectra of the clearcoat recorded. The amount of photooxidation was generically quantified using the Δ(–OH,–NH)/–CH] method, which ratios the absorbance in the 3800–2000 $cm^{-1}$ region to that in the 3100–2800 $cm^{-1}$ region [16,17].

## 3. Results

The continuous stress relaxation curves for Mel′-A and Mel′-N without HALS or UVA are shown in Fig. 4, where the vertical axis is the force at any time in the experiment normalized to the initial force. In the presence of UV light Mel′-A relaxes at a rate roughly 2.5 times that of Mel′-N, in accordance with the rates measured by chemical composition changes, such as carbonyl growth or hydroperoxide concentration. After less than 250 h of exposure, less than 10% of the original crosslinks remain in Mel′-A. The relaxation data for both Mel′-A and Mel′-N in the absence of light is shown for comparison. Both clearcoats relax at the same slow rate in the absence of UV light.

In Fig. 5 the intermittent relaxation curves for additive-free Mel′-A and Mel′-N are shown. These curves reflect the net changes in the polymer network. The vertical axis is the force at the end of a given strain pulse normalized to the force at the end of the first strain pulse and is proportional to the crosslink density. Mel′-N undergoes an initial increase in crosslink density followed by a steady decrease, while Mel′-A initially undergoes mainly crosslink scission. After approximately 800 h the rates of crosslink scission and formation are comparable, the crosslink density plateaus, and with continued exposure the crosslink density of Mel′-A begins to rise [26].

When Tinuvin 123 and/or Tinuvin 900 are added to the clearcoats their photooxidation behavior changes, in some cases dramatically. Fig. 6 shows the continuous relaxation behavior of Mel′-A with various levels of each additive. Additive-free Mel′-A relaxes rapidly. The addition of Tinuvin 123 slows the rate of crosslink/chain scission significantly, and surprisingly there is no difference between the formulation containing 0.25 and 1.5% by weight of Tinuvin 123. The addition of 1% by weight Tinuvin 123 and 1% of Tinuvin 900 (UVA) slows the rate of relaxation even more dramatically. The addition of Tinuvin 123 and/or Tinuvin 900 to Mel′-N also slows its rate of photooxidation, as measured by continuous stress relaxation (Fig. 7). The addition of either 0.25% Tinuvin 123, 1.0% Tinuvin 900, or 1%Tinuvin 123 and Tinuvin 900 slows the crosslink/chain scission rate approximately the same amount. When Mel′-A and Mel′-N contain both 1% Tinuvin 123 and 1% Tinuvin 900, their rate of chain/crosslink scission is low and approximately equal.

The intermittent relaxation results are shown in Fig. 8 for Mel′-A. The normalized force values on the vertical axis are proportional to the crosslink density of the network. The unstabilized version decreases in crosslink density at the onset of exposure, plateaus, and then finally increases in crosslink density as exposure continues (also shown in Fig. 5). The addition of 0.25% of Tinuvin 123 slows the rate of crosslink density loss. However, the addition of 1.5% Tinuvin 123 to Mel′-A leads to a faster decrease in crosslink density than the 0.25% clearcoats. Neither of the HALS containing clearcoats show the upturn in crosslink density that the unstabilized version shows. The addition of both Tinuvin 123 and Tinuvin 900 to Mel′-A slows the rate of crosslink density decrease to the same rate as the formulation containing only 0.25% Tinuvin 123. The effects of HALS and UVA on Mel′-N are more straightforward (Fig. 9). The addition of either Tinuvin 123 or Tinuvin 900 removes the initial increase in crosslink density seen in absence of additives, after which

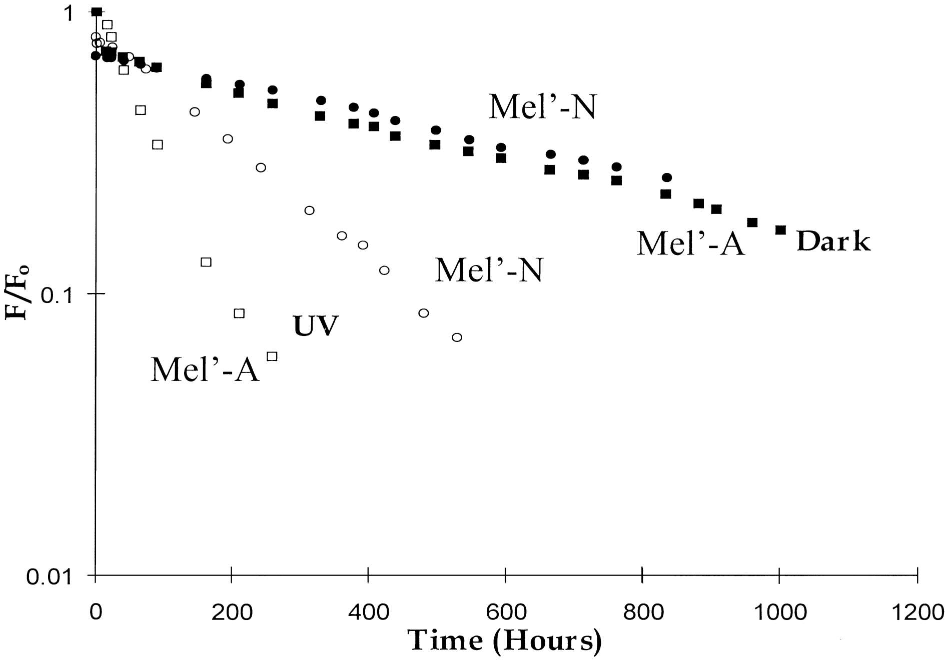

Fig. 4. Continuous stress relaxation of Mel′-A and Mel′-N. Upper curves for dark experiments, lower curves for experiments in UV radiation.

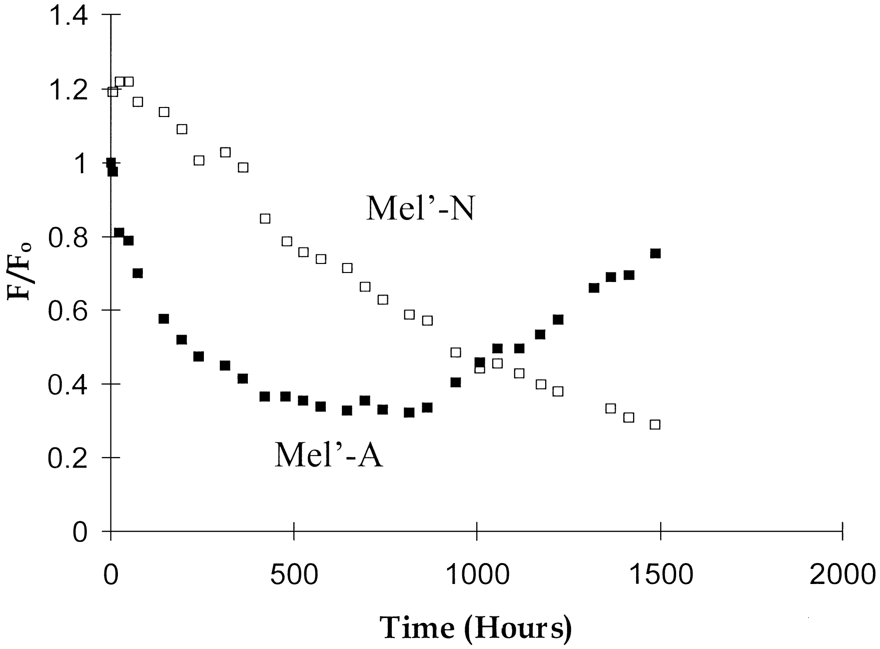

Fig. 5. Intermittent relaxation behavior of Mel′-A and Mel′-N in UV radiation. Vertical axis is proportional to crosslink density.

all of the variously stabilized versions lose crosslink density at roughly the same rate as the unstabilized version.

The infrared spectra of the coated silicon discs exposed next to the relaxation specimens were recorded periodically as a function of exposure. The Δ(–OH,–NH)/–CH] ratio was measured from each spectra and is plotted as a function of exposure time for Mel′-A in Fig. 10. In the absence of additives, the photooxidation rate of Mel′-A, as measured by the Δ(–OH,–NH)/–CH] method, is the largest. The addition of either a small or large amount of Tinuvin 123 slows down the initial rate of photooxidation equally (by a factor of 2–2.5). At longer times the degree of inhibition is smaller for all the formulations, with the amount of photooxidation at 2000 h of exposure differing only by a factor of 1.4 for the unstabilized and the Tinuvin 123 stabilized clearcoats.

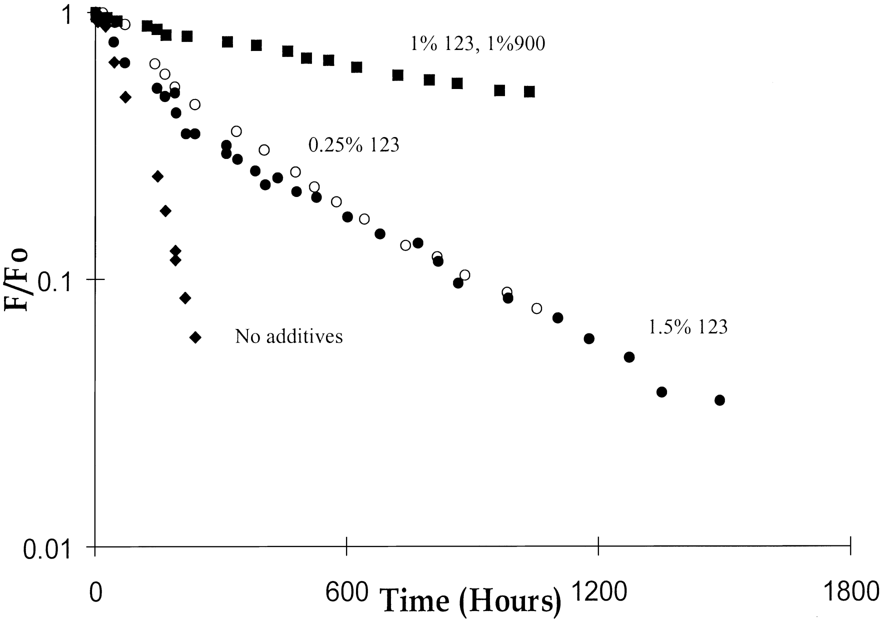

Fig. 6. Continuous relaxation behavior of Mel′-A with various additive levels.

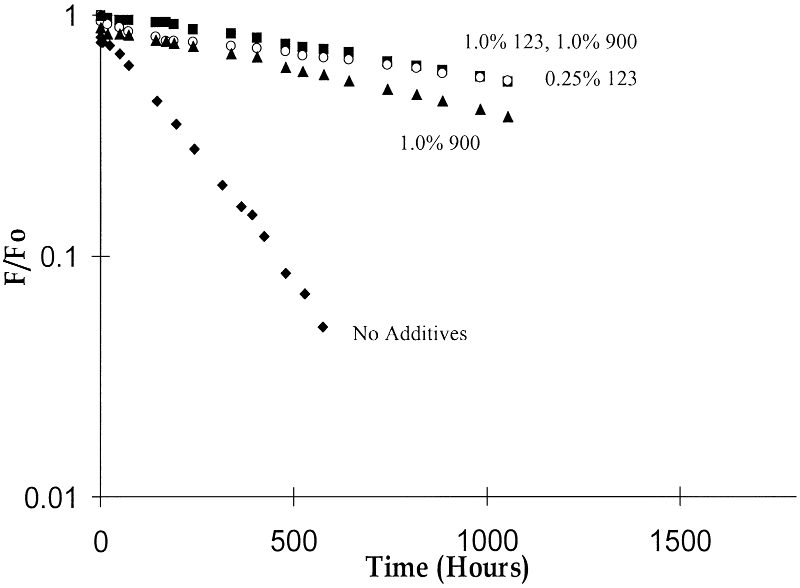

Fig. 7. Continuous relaxation behavior of Mel′-N with various additive levels.

The addition of Tinuvin 900 and Tinuvin 123 to Mel′-A inhibits the rate of photooxidation further.

## 4. Discussion

Chemical stress relaxation can clearly be used to discern differences in the photooxidation behavior of Mel′-A and Mel′-N. In addition, the effects of HALS and UVA on the chemical stress relaxation behavior of these clearcoats are also evident. However, these effects are complex, and a number of points in particular merit discussion, including: (1) the correspondence between chemical stress relaxation results and changes in network structure; (2) the slower rate of continuous relaxation when Tinuvin 123 is added to Mel′-A; (3) the equally slow rate of continuous relaxation when 0.25 and 1.5% Tinuvin 123 is added to Mel′-A; (4) the slower rate of continuous relaxation when either Tinuvin 123 or Tinuvin 900 is added to Mel′-N; (5) the different intermittent relaxation behavior of Mel′-A when different amounts of Tinuvin 123 are added; (6) the different

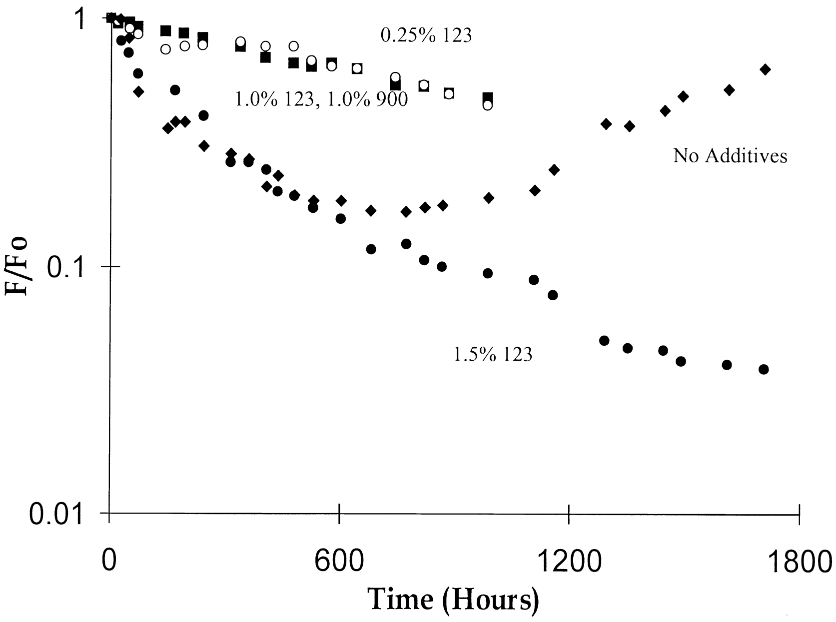

Fig. 8. Intermittent relaxation behavior of Mel′-A with various additive levels.

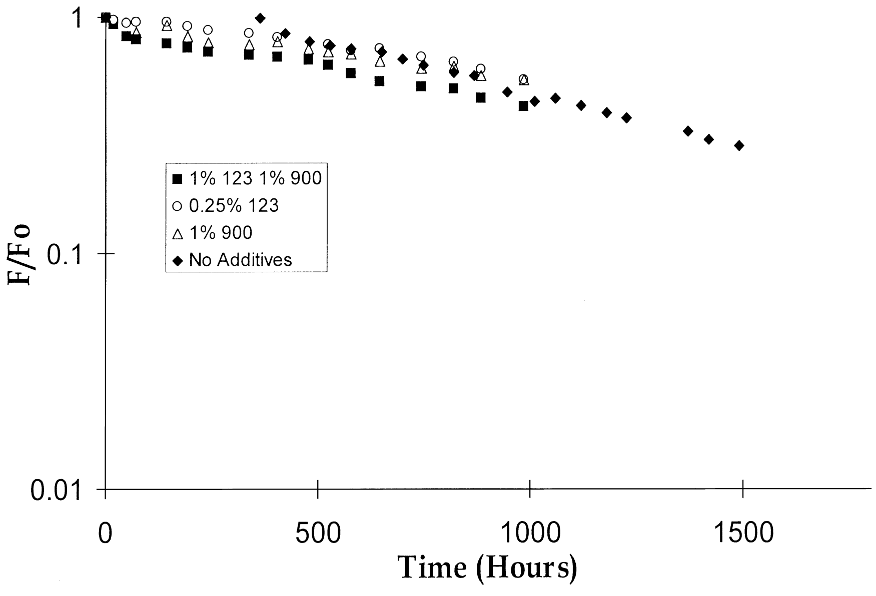

Fig. 9. Intermittent relaxation behavior of Mel′-N with various additive levels. Initial increase in crosslink density of unstabilized formulation not shown. Formulations shown in legend.

intermittent relaxation behavior of Mel′-N when Tinuvin 123 or Tinuvin 900 is added; and (7) the correlation between chemical composition changes observed in the infrared spectra and the chemical stress relaxation results.

Before discussing the chemical stress relaxation behavior of Mel′-A and Mel′-N in detail, a brief explanation of why these relaxation experiments can be used to measure changes in network parameters is required. Above their $T_g$, polymer networks can be modeled as rubber-like materials. The difference between these highly crosslinked coatings and classical room-temperature elastomers is the spacing between crosslinks. In elastomers the crosslink density is quite low, while in these clearcoats the crosslink density is on the order of $10^{-3}$ mol/cc, 2 orders of magnitude higher than in conventional elastomers. The statistical theory of rubber elasticity relates the rubbery modulus to the crosslink density, $\nu$,

$$\nu = \frac{E}{3RT}$$

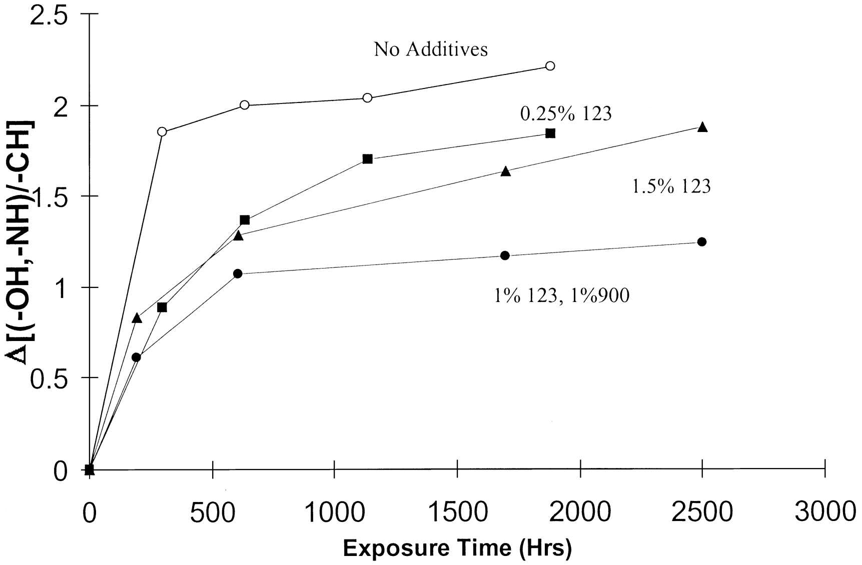

Fig. 10. Change in the (–OH,–NH)/–CH] ratio of the FTIR spectrum of Mel′-A with various additive levels.

where $E$ is the elastic modulus, $R$ is the universal gas constant and $T$ is the absolute temperature [29]. Thus, if the stiffness (modulus) of a rubbery material is measured at a known temperature, the crosslink density can be calculated. In these relaxation experiments the rubbery modulus is the load at any time in the experiment divided by the strain and the cross-sectional area of the specimen. In a continuous relaxation experiment the load will constantly decrease and, therefore, the modulus will constantly decrease. The rate of decrease in load is directly proportional to the rate at which crosslinks/chains are being broken. The above theory was initially developed for elastomers. However, many of the assumptions used to develop the theory are violated for highly crosslinked coatings. Hill has shown that the theory does, in fact, work well in spite of the violated assumptions, and therefore, linking continuous relaxation rates to rates of crosslink/chain scission and intermittent relaxation rates to crosslink density change rates is warranted [22–24].

The manner in which Mel′-A and Mel′-N degrade on exposure to UV radiation and humidity is clearly different. In the absence of UV light, but the presence of heat and humidity, Mel′-A and Mel′-N undergo crosslink/chain scission at approximately the same rate (Fig. 4). This rate is approximately equal to the expected rate of chain/crosslink scission due to hydrolysis at this temperature. In the presence of UV light both Mel′-A and Mel′-N undergo a higher rate of crosslink/chain scission, with Mel-A losing crosslinks approximately 2.5 times as fast as Mel′-N. This difference in rates is in agreement with previous results using various measures of chemical composition change, where Mel-A′s rate of photooxidation was observed to be approximately 2–3 times as fast as that of Mel-N [6]. The increased rate of crosslink/chain scission during UV exposure is thought to be due to free radical-driven photooxidation, although others have attributed this increased rate to photo-enhanced hydrolysis [30].

The addition of either 1.5 or 0.25% Tinuvin 123 to Mel′-A decreases the rate of crosslink/chain scission by a factor of 4.5 over the additive-free formulation (Fig. 6). Previous results using infrared spectroscopy have indicated a decrease in the rate of photooxidation, as measured by carbonyl growth, when Tinuvin 770 HALS is added to Mel-A. The decrease in photooxidation rate was approximately proportional the concentration of Tinuvin 770, ranging from a factor of 1.3 for 0.5% Tinuvin 770 to 2.6 for 2% Tinuvin 770 [31]. However, the Tinuvin 770 was more effective at inhibiting photooxidation at short exposure times than during long exposures. Rates of crosslink scission in Mel-A with and without Tinuvin 770 were also measured by following the disappearance of the 915 $\text{cm}^{-1}$ methoxy band, which has been reported to be proportional to the concentration of ether crosslinks in these clearcoats [4]. Again, the addition of Tinuvin 770 HALS slows the rate of disappearance of this band in proportion to the concentration of Tinuvin 770. Those infrared spectroscopy results are in some ways similar to what is reported here, in that Tinuvin 123 appears to inhibit photooxidation better for short exposures than for long exposures. However, the previous infrared results differ from those reported here using the Δ(–OH,–NH)/–CH] method (Fig. 10), in that the inhibition of photooxidation appears to be relatively independent of Tinuvin 123 concentration, in agreement with the continuous relaxation data. Loss of the 915 $\text{cm}^{-1}$ methoxy band in the present experiments is also in qualitative agreement with the Δ(–OH,–NH)/–CH] method results. The methoxy band absorbance decreases to zero in less than 150 h of exposure for additive free Mel′-A, while it still retains 25% of its absorbance after the same exposure for Mel′-A containing either 0.25 or 1.5% Tinuvin 123. Note that for all the formulations the infrared results indicate that the number of crosslinks remaining after even short exposures is quite low, in agreement with the continuous relaxation results.

Differences between the present results and previous studies in the amount of inhibition and the effect of HALS concentration may be due to the difference in analysis techniques [Δ(–OH,–NH)/–CH] vs. carbonyl growth] and also to the higher exposure temperatures in the present experiments (80°C), as opposed to the "near-ambient" (40°C) conditions used in previous studies. The higher temperatures may preferentially bias the photooxidation process towards chain/crosslink scission as opposed to attack on side chains or pendant groups. In addition, the methoxy band previously used to monitor crosslink scission is only sensitive to the loss of crosslinks, while the relaxation experiments used here are also sensitive to the rupture of backbone chains not associated with the crosslinks. Two final differences between the two groups of experiments is the lack of PTSA in the clearcoat formulation of the previous study and a difference in crosslinker (fully alkoxylated versus partially alkoxylated). Thus, exact correlation between the previous results and those reported here should not necessarily be expected.

Mel′-N also undergoes a decreased rate of crosslink/chain scission when Tinuvin 123 and/or Tinuvin 900 are added to the formulation; the rate being reduced approximately to the rate of hydrolysis regardless of the additive concentration (Fig. 7). Because the end groups in Mel′-N do not absorb UV light, the photooxidation that occurs must be initiated at other locations within the clearcoat. For example, Binns et al. have reported on the scission of melamine crosslinker by the absorption of UV light as a primary photochemical event, other moieties within the clearcoat must also be capable of absorbing UV light [32]. Primary photooxidation events cannot be hindered by the addition of HALS, however, free radical chain propagation can, and thus the addition of Tinuvin 123 appears to decrease the rate of chain scission by a factor of almost 10, in effect reducing the rate of scission to that produced by hydrolysis alone. Both Tinuvin 123 and the combination of Tinuvin 123 and Tinuvin 900 appear to reduce the rate of photooxidation the same amount as measured by continuous relaxation. Using the Δ(–OH,–NH)/–CH] (data not shown) the effect of adding either Tinuvin 123 and/or Tinuvin 900 is much less dramatic, and the inhibition factor is less than 1.3. Previously Tinuvin 770 HALS was observed to have no effect upon the photooxidation behavior of Mel-N, that is, the clearcoat's rate of photooxidation, as measured by carbonyl growth could not be slowed by the addition of HALS. Yet here, clearly the rate of continuous relaxation is slowed significantly by the addition of even small amounts of Tinuvin 123. Thus, the two IR measurements are in much closer agreement than the relaxation results and the IR results. Reasons for the disparity between this work and previous work is unknown but again may be related to the different experimental conditions (temperatures) and the different formulation (Tinuvin 770 vs. Tinuvin 123 and no PTSA vs. 0.3% PTSA).

HALS also have a dramatic effect on the rate at which crosslinks form. A simple view of the mode of action of HALS indicates that the presence of HALS will allow for reaction (1) below as a mechanism of termination, reducing the likelihood of reaction (2).

$$P^{\bullet} + {>}NO^{\bullet} \Rightarrow NOP \text{ (no crosslink)} \tag{1}$$

$$P^{\bullet} + P^{\bullet} = PP \text{ (crosslink)} \tag{2}$$

The intermittent relaxation data supports this simple reaction scheme (Fig. 8) for Mel′-A. Additive free Mel′-A undergoes first a decrease in crosslink density as the rate of crosslink/chain scission is quite high (Fig. 4), then the crosslink density plateaus as the rates of crosslink scission and formation are equal, and finally the crosslink density increases as the rate of crosslink formation exceeds the rate of crosslink/chain scission. When 1.5% Tinuvin 123 is added to Mel′-A (Fig. 8) the crosslink density continuously decreases, no upturn is observed — indicating a reduction in the rate of crosslink formation due to radicals that would have terminated to form crosslinks now terminating with nitroxyl radicals.

When 0.25% of Tinuvin 123 is added to Mel′-A the overall changes in crosslink density are much smaller. However, because the rates of crosslink/chain scission in Mel′-A with both 0.25% and 1.5% Tinuvin 123 are the same, the smaller changes in crosslink density must be due to a higher rate of crosslink formation in Mel′-A containing only 0.25% Tinuvin 123. This results in the non-intuitive conclusion that the addition of less Tinuvin 123 to Mel′-A gives rise to smaller changes in the crosslink density than in Mel′-A containing more Tinuvin 123. It should be noted, however, that the polymer network of Mel′-A containing 0.25% Tinuvin 123 is quite dynamic, with many crosslinks being formed and broken, while the crosslink structure in Mel′-A containing 1.5% Tinuvin 123 is much more static. Thus, a high concentration of Tinuvin 123 dramatically slows the rate of crosslink/chain scission and also the rate of crosslink formation, while low concentrations of Tinuvin 123 dramatically slow the rate of scission but have only a minor effect on the rate of crosslink formation. Also of note, is that the rate of change of crosslink density for Mel′-A containing both Tinuvin 123 and Tinuvin 900 is the same as the rate for Mel′-A containing only 0.25% Tinuvin 123. In this case, the Mel′-A formulation containing both UVA and HALS undergoes very little chemical change, mostly hydrolysis, as its rate of crosslink scission has been shown to be quite low (Fig. 6). Thus, two formulations (0.25% Tinuvin 123 and 1% Tinuvin 123 plus 1% Tinuvin 900) one undergoing almost no chemical change, and one undergoing a great deal of chemical change have the same rate of change of crosslink density.

In Mel′-A the addition of 0.25% Tinuvin 123 not only slows the rate of crosslink formation compared to the additive free version, but reduces it to zero. This can be demonstrated as follows. If a clearcoat degrades by crosslink scission alone, with no concurrent crosslink formation, then the continuous relaxation experiment and the intermittent relaxation experiment will measure the same quantity, i.e. the rate of crosslink scission, since no crosslink formation would be included in the intermittent relaxation results. Thus, the difference between the intermittent relaxation curves and the continuous relaxation curves is the formation of crosslinks [33]. When both the intermittent and continuous relaxation data for Mel′-A containing 1.5% Tinuvin 123 and additive free Mel′-A are superimposed, as in Fig. 11, the intermittent and continuous relaxation curves for Mel′-A containing 1.5% Tinuvin 123 superimpose. This does not occur for additive-free Mel′-A or Mel′-A containing 0.25% Tinuvin 123; the difference between those intermittent and continuous curves being the amount of crosslink formation. The results highlight a subtle, but important, implication of these experiments: small changes in the stabilizing formulation (different amounts or, perhaps, different types of HALS or UVAs) can profoundly change the final mode of degradation in a manner that would not be anticipated by chemical composition change measurements, which can in turn significantly influence the long-term weathering performance of clearcoats.

The addition of Tinuvin 123 and/or Tinuvin 900 to Mel′-N has only a small effect on the exposure-induced changes in the crosslink density. The initial increase in crosslink density observed in the additive free formulation of Mel′-N is removed, after which the rate of crosslink loss is the same regardless of formulation. The inhibition of the initial increase in crosslink density by either HALS or UVA indicates that the origin of that increase is photochemical in nature, and not the result of continuing thermal cure. The additive free formulation of Mel′-N apparently undergoes a higher proportion of crosslink scission than crosslink formation as there is a significant difference between the continuous and intermittent relaxation curves. However, the addition of either Tinuvin 123 or Tinuvin 900 slows the rate of scission to that expected by hydrolysis and apparently reduces the already small rate of crosslink formation to zero (indicated by the overlap of the continuous and intermittent relaxation curves for the additive containing formulations).

As a final note, it appears that the rate of photooxidation as measured by the Δ(–OH,–NH)/–CH] method agrees qualitatively with the rates of crosslink scission, but not the overall changes in crosslink density. Because the balance of weathering-induced chain/crosslink scission to weathering-induced crosslink formation

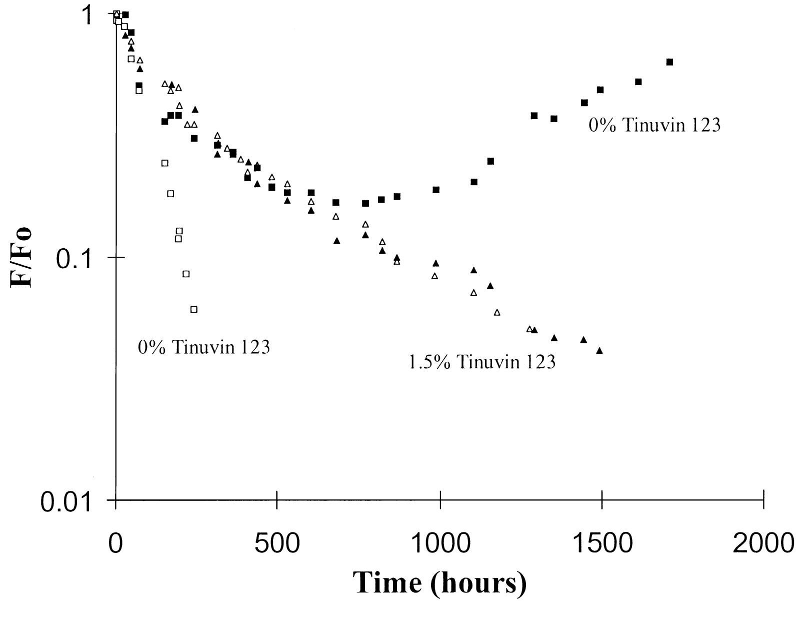

Fig. 11. Intermittent and continuous relaxation behavior of Mel′-A with 0 and 1.5% HALS. Curves as indicated on graph. Intermittent relaxation: filled symbols, continuous relaxation: open symbols.

can have a profound effect on potential clearcoat failure mechanisms, ranking clearcoats and assessing additive effectiveness by measuring photooxidation alone carries some risk.

## 5. Conclusions

Chemical stress relaxation experiments demonstrate that the mode of photooxidation in two similar acrylic/melamine clearcoats is quite different. When formulated without HALS or UVA Mel′-A tends to increase in crosslink density after an initial decrease in crosslink density, while Mel′-N decreases in crosslink density after an initial increase. The addition of hindered amine light stabilizers changes the mode of degradation of Mel′-A dramatically — slowing the rate of crosslink/chain scission and, for higher concentrations of HALS, halting the formation of crosslinks. Mel′-N is more easily stabilized due to its inherent photooxidative stability. These measurements agree generically with the rates of photooxidation observed in these coatings using techniques that measure chemical composition changes, such as FTIR or ESR. However, chemical stress relaxation gives added insight into the pathways of degradation and the effect HALS can have on the balance of reaction in these coatings.

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