EFFECTS OF RELATIVE HUMIDITY ON
PHOTODEGRADATION OF ACRYLIC MELAMINE COATINGS;
A QUANTITATIVE STUDY

by

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EFFECTS OF RELATIVE HUMIDITY ON PHOTODEGRADATION OF ACRYLIC MELAMINE COATINGS: A QUANTITATIVE STUDY

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Introduction
This study is part of an effort to generate experimental data for validating a reliability-theory approach to predict the service life of polymeric coatings (1). This approach is based on the effective dosage model, relating damage by radiation dosage absorbed in the coating through the quantum yield. This parameter depends not only on physical and chemical properties of the material but also strongly on environmental factors, such as moisture and temperature. To provide data for validating the effective dosage model, the effects of over 200 different combinations of exposure conditions of ultraviolet light, temperature, and relative humidity on the photodegradation of coatings have been investigated. In a previous publication, we have presented the methodology to measure and calculate the absorbed dosage and apparent quantum yield over a wide range of exposure conditions using FTIR and UV-visible spectrometers (2). Factors critical to the accuracy and reproducibility of these quantities include UV-visible absorption characteristics of the coating, degradation products, and dose UV-visible spectra processing, and reproducibility of UV-visible and FTIR spectrometers. The effects of relative humidity (RH) on the apparent quantum efficiency and the magnitudes and rates of photodegradation and moisture-enhanced photolysis of a partially-methylated melamine acrylic coating are presented in this paper. Partially-methylated melamine acrylate coating was one of the materials chosen for study.

Experimental
A model acrylic melamine coating consisting of a mixture of a hydroxy-terminated acrylic polymer and a partially-methylated amine resin was used. The ratio of acrylic resin to melamine crosslinking agent was, by mass, 70:30. Coatings were layered on CaF<sub>2</sub> substrates by spin coating. The films were then cured at 130 °C for 20 min, all coated samples were well cured. The coating thickness was 10 ± 2 μm and was uniform over the entire coated surface. Complete details of the instrumentation used in this study are described elsewhere (2). Briefly, the experimental setup consisted of 12 light simulators, exposure cells, and various controlling systems and instruments. Coated CaF<sub>2</sub> samples were placed in an exposure cell, which consisted of 12 windows corresponding to the 12 exposure conditions. Ten of the windows contained narrow bandwidth filters covering radiation from 290 nm to 525 nm, one was completely covered, and one was left open without a filter designated as "full UV". A quartz disk was placed directly underneath the filter and above the coated CaF<sub>2</sub> plate. Each cell contained an inlet and an outlet to allow air with the desired temperature and RH to circulate in the space between the quartz and the coated-CaF<sub>2</sub> plate. Temperature and humidity sensors connected to each cell and to a computer were used to control temperature and RH in each cell.

Nominal RHs of <1% (dry), 20%, 40%, 70%, and 90% at normal temperatures of 20 °C, 40 °C, 50 °C, and 60 °C and 17 different UV conditions were selected. The relative humidity in each cell was provided by a specially-designed RH generator, which controlled RHs in the 0% to 90% range to within ±3% by controlling the ratio of dry air and moisture-saturated air. The temperature in each cell was maintained within ±2 °C of the desired value. The radiation source was supplied by two 1000 W xenon arc solar simulators, which provided infrared-free, near ambient temperature (24 °C) radiation of wavelengths between 275 nm and 800 nm. A UV-visible spectrometer equipped with a fiber-optics sensor and connected to a robotic controlling system was used to measure the irradiance at each of the 12 windows. UV-visible and IR absorbance spectra of the coating as a function of exposure were measured using UV-visible and FTIR spectrometers in front of an automated sampler. The automated sampling device allowed unattended, efficient, and quick recording of the UV and IR absorbance spectra of the coating specimens at all locations. At each specified time interval, the coated CaF<sub>2</sub> plate was removed from the exposure cell, fitted into a deaeration unit on the automated sampler, and UV and IR spectra were collected. UV-visible spectra were recorded from 100 nm to 820 nm with a resolution of 2 nm at 2× per scan. FTIR spectra were the average of 128 scans, which were recorded at a resolution of 4 cm<sup>-1</sup> using a liquid nitrogen-cooled MCT detector and a purge air. Data on irradiance and cooling were used to calculate the absorbed dosage in the coating.

A computer program was written to estimate absorbed dosage, damage, and quantum yield using inputs provided by UV-visible and FTIR measurements. The apparent quantum yield in this study is expressed as a change in FTIR intensity per unit thickness per amount of radiation absorbed in the coating. If FTIR intensity for the degradation is expressed as absorbance (A), thickness in meter (m), and radiation absorbed by the coating in joules (J), the apparent quantum yield is expressed in A m<sup>-2</sup>J<sup>-1</sup>. Absorption coefficients of relevant IR bands are being measured to convert IR absorbance units into functional group concentration. Only the results of the effects of RH on photodegradation in the full UV at 30 °C are presented in this paper.

Results and Discussion
FTIR difference spectra (spectra of exposed specimen-spectrum before exposure) of the acrylic melamine coatings after exposure 2010 h under different RHs in "full UV/50 °C condition are displayed in Figure 1. Decreases in FTIR intensity were observed in the 2750 cm<sup>-1</sup>-3100 cm<sup>-1</sup> range for all of the exposure conditions, and increases in intensity occurred in 3100 cm<sup>-1</sup>-3400 cm<sup>-1</sup> range. Several new bands appeared, including those 1760 cm<sup>-1</sup> (amide I), 1670 cm<sup>-1</sup> (amide II), and 1630 cm<sup>-1</sup> (amide III). The bands associated with the acrylic resin, e.g., 1730 cm<sup>-1</sup> (C=O), 1175 cm<sup>-1</sup> (ester C-O), which were essentially unaltered in the absence of light even at high RH (3), also changed substantially with UV exposure. Figure 2 depicts how RH changes with exposure time for the H<sup>1</sup> cm<sup>-1</sup> (chain scission) and 1670 cm<sup>-1</sup> (oxidation) bands of the coating at 1 RHs under the UV/50 °C condition. Both the rate and magnitude of the degradation modes increased with increasing RH. The total intensity change at 100% RH was due to four different degradation processes: post cure (PC) reactions, dark hydrolysis due to the RH (H),photolysis (P) and moisture-enhanced photolysis (MEP). Photolysis was the major contributor to all of these processes, while the second most significant was moisture-enhanced photolysis (MEP). The experiments were conducted so that these processes were measured individually. In this way, the effects of RH on the rate and magnitude of each of these processes of a partially-methylated melamine acrylic coating could be quantified. Selective data are presented in Table 1 and Figure 3. More complete results are given elsewhere (3).

Table 1. Effects of RH on Total Degradation (T) and Moisture-enhance Photolysis (MEP) Rates for Different Functional Groups of the Coating Exposed to UV/50 °C. (Rates, dA/dt, are Measured from the Initial Slope of, e.g., the Curves Given in Figure 2)

<table>
<thead>
<tr>
<th>Wave No. (cm&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>0% RH</th>
<th>19.2% RH</th>
<th>72.7% RH</th>
<th>90.8% RH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1065</td>
<td>0.86</td>
<td>1.86</td>
<td>3.52</td>
<td>4.45</td>
</tr>
<tr>
<td>1175</td>
<td>0.46</td>
<td>0.53</td>
<td>1.14</td>
<td>1.64</td>
</tr>
<tr>
<td>1670</td>
<td>0.95</td>
<td>2.16</td>
<td>3.94</td>
<td>4.97</td>
</tr>
</tbody>
</table>

Since the degradation due to PC was very small, the total rate value at 0% RH condition represents the rate of photolysis of the coating. Both the magnitudes and rates of the rates and extent of total degradation were greater than those of the PC, P, and H combined. This difference [T-(H+P+PC)] is tenfold as moisture-enhanced photolysis because the enhancement is caused by moisture present in the film. Formaldehyde released during hydrolysis which acts as a sensitizer, is believed to be responsible for the enhancement (3). Both the magnitudes and rates of moisture-enhanced chain scission oxidation, and ester side chain cleavage increased with increasing RH. However, the rates of the chain scission enhancement at all RHs observed in this study are smaller than those reported previously (5,6).

The apparent quantum yield was determined from the initial portio of the IR intensity (damage)absorbed dosage curves shown in Figures 4a and 4b for chain scission and oxidation, respectively. A first order polynomial function was used to fit the damage/dosage curve to obtain the quantum yield values. The presence of moisture appeared to incr
At 90% RH, the quantum efficiency of RH on the photodegradation and quantum yield of partially-methylated melamine acrylic coating exposed to 50°C was observed.

The effects of RH on each process were studied, which showed a significant reduction in the photodegradation, chain scission, and moisture-enhanced processes with increasing RH. Also, moisture appeared to increase the quantum efficiency of acrylic melamine coatings.

References:


Figure 2: Chain scission (1085 cm⁻¹ band) (a) and oxidation (1670 cm⁻¹ band) (b) as a function of time for a partially-methylated melamine acrylic coating exposed to different relative humidities under "full UV+50°C" condition.

Figure 3: FTIR intensity changes for post-curing (PC), photolysis (P), hydrolysis (H), and moisture-enhanced photolysis (MEP) for chain scission (a) and oxidation (b) of a partially-methylated melamine acrylic coating exposed to different relative humidities under "full UV+50°C" condition (data taken at 14d).

Figure 4: Chain scission (1085 cm⁻¹ band) (a) and oxidation (1670 cm⁻¹ band) (b) as a function of absorbed dosage of a partially-methylated melamine acrylic coating exposed to different relative humidities under "full UV+50°C" condition (only changes due to P and MEP are included).