Amine-Quinone Polymers and the Protection of Metals Against Corrosion

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Back to the Future!

We began working on amine-quinone polymers in 1991 as a means of protecting commercial iron particles against corrosion.

Indeed we demonstrated amine-quinone polyurethanes protect commercial particles against corrosion.

Jeng-Li Liang and David E. Nikles "Amine-Quinone Polyurethanes as Binders for Metal Particle Tape" *IEEE Transactions on Magnetics* 1993, 29(6), 3649-3651.

We also demonstrated these polymers could replace the ceramic coatings used to protect the iron particles against corrosion.


Here we examine the use of radiation-curable amine-quinone polyurethanes as potential dispersing agents for commercial iron particles in solventless acrylate formulations.
Objectives

Synthesize new radiation curable amine-quinone polyurethanes

Demonstrate that these polymers can promote the dispersion of commercial iron particles in liquid acrylates

Demonstrate that these polymers protect commercial iron particles against corrosion

Demonstrate that these polymers protect metals against corrosion
Synthesis of Amine-Quinone Polyurethane with Acrylate Groups in the Side Chain

\[
\text{HO-}{\text{HC-}}\text{H}_2\text{C-}O\text{-}{\text{O}}\text{-CH}_2\text{-CH}_2\text{-OH} + \text{HO-}R\text{-OH} + \text{HO-CH}_2\text{-CH}_2\text{-OH} \rightarrow  \text{DMF/45-50}^\circ\text{C/24h}
\]

\[
\text{HO-}{\text{HC-}}\text{H}_2\text{C-}O\text{-}{\text{O}}\text{-CH}_2\text{-CH}_2\text{-OH} + \text{HO-CH}_2\text{-CH}_2\text{-OH} \rightarrow  \text{DMF/45-50}^\circ\text{C/24h}
\]

THE UNIVERSITY OF ALABAMA
Center for Materials for Information Technology
an NSF Materials Science and Engineering Center
**Synthesis Of Amine-Quinone Polyurethane with Acrylate Groups in the Side Chain**

<table>
<thead>
<tr>
<th>Sr #</th>
<th>POLYURETHANES</th>
<th>HO-R-OH</th>
<th>M&lt;sub&gt;n&lt;/sub&gt;</th>
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<tbody>
<tr>
<td>1</td>
<td>AQPUDA-1</td>
<td>HO(CH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;O)&lt;sub&gt;n&lt;/sub&gt;H</td>
<td>400</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(PEG 400)</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>AQPUDA-2</td>
<td>HO(CH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;O)&lt;sub&gt;n&lt;/sub&gt;H</td>
<td>650</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(Terathane 650)</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>AQPUDA-3</td>
<td>H[(OCH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;5&lt;/sub&gt;C(=O)]&lt;sub&gt;n&lt;/sub&gt;OCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;OCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;O[C(=O)(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;O]&lt;sub&gt;n&lt;/sub&gt;H</td>
<td>1250</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(Polycaproactone diol)</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>AQPUDA-4</td>
<td>HO(CH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;O)&lt;sub&gt;n&lt;/sub&gt;</td>
<td>404</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(OCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;n&lt;/sub&gt;OH</td>
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### Physical Properties of Synthesized Amine-Quinone Polyurethanes

<table>
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<tr>
<th>Sr. #</th>
<th>Copolymer</th>
<th>AQM-1&lt;sup&gt;a&lt;/sup&gt; (%)</th>
<th>Acrylate&lt;sup&gt;a&lt;/sup&gt; (%)</th>
<th>η&lt;sub&gt;inh&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt; (dL/g)</th>
<th>T&lt;sub&gt;g&lt;/sub&gt;&lt;sup&gt;c&lt;/sup&gt; (°C)</th>
<th>T&lt;sub&gt;d&lt;/sub&gt;&lt;sup&gt;d&lt;/sup&gt; (°C)</th>
<th>Residue&lt;sup&gt;d&lt;/sup&gt; (%)</th>
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<tbody>
<tr>
<td>1</td>
<td>AQPUDA1</td>
<td>12</td>
<td>22</td>
<td>0.24</td>
<td>12</td>
<td>184</td>
<td>236</td>
</tr>
<tr>
<td>2</td>
<td>AQPUDA-2</td>
<td>43</td>
<td>24</td>
<td>0.48</td>
<td>17</td>
<td>186</td>
<td>217</td>
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<tr>
<td>3</td>
<td>AQPUDA-3</td>
<td>24</td>
<td>20</td>
<td>0.24</td>
<td>-</td>
<td>223</td>
<td>261</td>
</tr>
<tr>
<td>4</td>
<td>AQPUDA-2</td>
<td>18</td>
<td>21</td>
<td>0.31</td>
<td>-</td>
<td>188</td>
<td>221</td>
</tr>
</tbody>
</table>

*Where a = By <sup>1</sup>H NMR using DMSO-d₆ as solvent, b = In DMF at 30 °C using a concentration of 0.5 g/dLc = Using DSC from the 1<sup>st</sup> heating run at a heating rate of 20 °C/min. and d = Using TGA at a heating rate of 20 °C/min.*
The amine-quinone polyurethanes were chemisorbed onto the commercial iron particles from cyclohexanone solution.

The surface treated particles were dispersed in propylene glycol diacrylate.
Comparative Corrosion Studies

Tape samples containing commercial iron particles
Exposed to pH 2.0 aqueous buffer
The samples having AQPUDA-1 showed no corrosion by pH 2.0 aqueous buffer
Radiation curable amine-quinone polymer protect commercial iron particles against corrosion
EIS Studies of Corrosion Protection of Metals by Radiation Curable Amine-Quinone Polymers

Bode plots for AQPUDA-2 films on iron, fig. 4a, or on Al-2024T3, fig. 4b, exposed to 0.1 M NaCl electrolyte. Circles — impedance curves, squares — phase angle curves. Fig. 4a, open symbols — initial curves, closed symbols — after 230 days exposure. Fig. 4b, open symbols — initial curves, closed symbols, after 8 days exposure.
Conclusions

Radiation curable amine-quinone polymers promote dispersion of commercial iron particles in liquid acrylates

The polymers protected commercial iron particles against corrosion by pH 2.0 aqueous buffer

The polymer protected iron and aluminum aircraft alloys against corrosion