QUANTITATION OF BURIED CONTAMINATION

BY USE OF SOLVENTS

Semi-Annual Report

for

January 1, 1972 through June 31, 1972

Supported by

NASA Grant NGR 35-001-012
Supplement No. 2

Submitted to the

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

by the

Department of Polymers and Coatings
North Dakota State University
Fargo, North Dakota 58102

Investigators: S. Peter Pappas, Paul Hsiao, and Loren W. Hill
Introduction

The objectives of the overall project are: (1) to develop non-sporicidal methods for solvent degradation of cured polymeric resins that are used in spacecraft, and (2) to determine whether reaction conditions during resin cure cause decontamination of the component that is being fabricated. The previous report described the application of solubility parameter methods to the degradation of amine cured epoxy resins. The present report describes studies on (1) the solubilization of cured silicone resins, and (2) spore viability on exposure to amine solvents as well as to a silicone resin (DC 840) dissolved in amine solvents.

Results and Discussion

A) Solubilization studies were carried out on various cured silicone resins prepared from Dow Corning materials - DC 801, 802, 803, 804, 805, 806a, 808, and 840 - as well as from a General Electric product - SR 112. The most comprehensive studies were carried out on DC840, some characteristics of which are presented in Scheme I, which also depicts the mechanism of heat-curing. Our initial approach was to prepare a solvent spectrum as is normally done in a solubility parameter study. However, in contrast to our experience with amine cured epoxy resins, it was found that complete dissolution of cured silicone resins could be achieved without extensive physical degradation of samples. Of a large variety of potential solvents, including hydro-
carbons, aromatics, ethers, esters, amides, and alcohols, only those containing a primary or secondary amine (RNH$_2$ or R$_2$NH) function were effective in causing dissolution of the cured silicone resins examined, i.e., the results were independent of solubility parameter. Tertiary amines (R$_3$N), pyridine, and an aromatic amine caused swelling of the resins, but did not effect solubilization. Furthermore, the presence of a hydrocarbon segment in the amine solvents facilitated the rate of dissolution. Representative results are presented in Table I. Viscosity measurements were conducted on the cured resins dissolved in amine solvents. It was found that the molecular weights derived from these measurements decreased as a function of time, which is indicative of degradation of the cured resin. Based on the specificity of the amine solvents and the viscosity measurements, we have elaborated a model which is depicted in Scheme II. The key features are: (1) a hydrocarbon segment in the amine facilitates penetration of the hydrocarbon-like outer layer of the cured silicone resins, and (2) appropriate amine solvents partially degrade the cured resin by forming silicone-nitrogen bonds at the expense of silicon-oxygen-silicon cross-linkages.

We have acquired some chemical evidence which provides support for this hypothesis. Of particular importance, we have found that if the amine solution of the cured silicone resin is applied to a panel, a hard coating with properties comparable to the heat-cured film results
when the amine is allowed to evaporate. This behavior is most reasonably interpreted as reflecting the reversal of the degradation step (see Scheme II), which is expected on thermodynamic grounds. In a practical sense, this finding is potentially applicable to the coating of heat-sensitive materials. In further support of the intermediacy of silyl amine fragments, we have found that p-nitrophenol becomes incorporated into the resin when heated together in the amine solvents. The p-nitrophenol incorporation is readily demonstrated by UV spectroscopy. Whereas control experiments in the absence of amines cannot be conducted on the cured resins due to their insolubility in all other classes of solvents, control experiments carried out on the precured resin provide support for this mechanism. The proposed trapping of the silyl amine intermediate is also depicted on Scheme II.

B) Based on the solubilization results, certain of the most effective amine solvents were selected for spore viability studies. Our initial investigations were conducted on an unknown strain of Bacillus subtilis obtained from Dr. Bayard Sleeper of our Bacteriology department. More recent studies have been carried out on spores of Bacillus subtilis var. Niger, obtained from NASA. The results with both samples appear to be comparable. Determination of spore viability after exposure to amines is being accomplished by the plate counting method. In each case, a ml of the spore solution (or broth) is diluted to 10 ml in amine solvent. The control is diluted in sterilized,
distilled water. After shaking, aliquots are removed as a function of time and further diluted in distilled water. One ml of each appropriately diluted sample is transferred to a Petri dish to which nutrient agar is added. After solidification of the agar, the dishes are inverted and incubated at 30°C for twenty four hours. The dilutions are made so that between 30 and 300 colonies result, which are counted by marking with a wax pencil. Each sample is plated and counted in duplicate. In one experiment, the amines also contained the dissolved resin. Most of the preliminary experiments resulted in recoveries on the order of 5 to 10% relative to controls. However, one experiment yielded considerably higher recoveries in the 30 to 80% range. On examining some of the variables more closely, including the temperature of heat-shock, the time spans at various stages of the spore preparation, and the heat evolved on adding the spores to the amines, it has become apparent that the most important factor is the amount of residual amine present in the plating procedure. Consequently, we have modified our procedure by removing the bulk of the amine prior to plating and thereby have achieved recoveries on the order of 80 to 90%. The amine, such as butylamine, b. p. 78°C, is removed after the first 10 fold dilution of the amine solution of the spores by applying an aspirator and carefully evaporating about 1/10th of the volume. On the basis of these results, it appears that the toxicity of amines is essentially a bacteriostatic effect rather than a bactericidal effect. The presence of the dissolved
resin in the amine solution appears to result in slightly improved recoveries.

References

Scheme I

Silicone Resins

Precured Resins

\[ R = \text{phenyl and methyl} \]

\[ \begin{align*}
\text{R} & \quad \text{R} \\
\text{Si} - \text{O} & \quad \text{Si} - \text{O} \\
\text{OH} & \quad \text{R}
\end{align*} \]

\[ \begin{align*}
\text{R} & \quad \text{R} \\
\text{Si} - \text{O} & \quad \text{Si} - \text{O} \\
\text{OH} & \quad \text{R}
\end{align*} \]

Dow Corning 840

average M. W. 2300

Phenyl/methyl - 1.2

about 5 OH groups/molecule

Cross-Linked

Cured Resins

\[ \begin{align*}
\text{R} & \quad \text{R} \\
\text{Si} - \text{O} & \quad \text{Si} - \text{O} \\
\text{O} & \quad \text{R}
\end{align*} \]

\[ \begin{align*}
\text{R} & \quad \text{R} \\
\text{Si} - \text{O} & \quad \text{Si} - \text{O} \\
\text{O} & \quad \text{R}
\end{align*} \]

+ H₂O

Insoluble in all solvents except amines

450°F

2 hours
Table I

Solubilization of Cured DC 840 Silicone Resin by Amines

(50 mg. in 2 ml. solvent)

Effect as a function of time

<table>
<thead>
<tr>
<th>Solvent</th>
<th>10 min.</th>
<th>2 hrs.</th>
<th>20 hrs.</th>
<th>68 hrs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethylamine</td>
<td>dissolved</td>
<td>dissolved</td>
<td></td>
<td></td>
</tr>
<tr>
<td>diethylamine</td>
<td>swollen</td>
<td>dissolved</td>
<td></td>
<td></td>
</tr>
<tr>
<td>butylamine</td>
<td>swollen</td>
<td>dissolved</td>
<td></td>
<td></td>
</tr>
<tr>
<td>piperidine</td>
<td>swollen</td>
<td>dissolved</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-ethyl-1,2-diaminoethane</td>
<td>swollen</td>
<td>dissolved</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,2-diaminopropane</td>
<td>swollen</td>
<td>dissolved</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,3-diaminopropane</td>
<td>no effect</td>
<td>sl. swollen</td>
<td>swollen</td>
<td>partly dissolved</td>
</tr>
<tr>
<td>1,2-diaminoethane</td>
<td>no effect</td>
<td>sl. swollen</td>
<td>swollen</td>
<td>swollen</td>
</tr>
<tr>
<td>pyridine</td>
<td>no effect</td>
<td>sl. swollen</td>
<td>sl. swollen</td>
<td>swollen</td>
</tr>
<tr>
<td>triethylamine</td>
<td>no effect</td>
<td>sl. swollen</td>
<td>sl. swollen</td>
<td>swollen</td>
</tr>
<tr>
<td>tetraethylenepentamine</td>
<td>no effect</td>
<td>no effect</td>
<td>sl. swollen</td>
<td>sl. swollen</td>
</tr>
<tr>
<td>N-methylaniline</td>
<td>no effect</td>
<td>no effect</td>
<td>sl. swollen</td>
<td>sl. swollen</td>
</tr>
</tbody>
</table>
Scheme II

Proposed Model for Resin-Amine Interaction

Cross-Linked Cured Resin

Resin in Amine Solution

\[
\begin{align*}
\text{Cross-Linked Cured Resin} & \quad \text{Resin in Amine Solution} \\
\{ -O-Si-O-Si - \} & \quad \{ -O-Si-O-Si - \} \\
+ R_2NH & \quad + \text{OH} \\
\end{align*}
\]

Trapping of Silylamine

\[
\begin{align*}
\{ -O-Si-O- \} & \quad \{ -O-Si-O- \} \\
\text{NR}_2 & \quad \text{OH-CH}_4-p-\text{NO}_2 \\
\end{align*}
\]

\( \lambda_{\text{max}} 300 \text{ nm} \)