Evaluation of Volatile Organic Compound Emission from the Preparation and Application of BoeGel-EP II

M. V. Henley
Air Force Research Laboratory – Tyndall Site
139 Barnes Drive, Suite 2,
Tyndall Air Force Base, Florida 32403-5323

139 Barnes Drive, Suite 2,
Tyndall Air Force Base, Florida 32403-5323

Approved for Public Release; Distribution Unlimited
NOTICES

USING GOVERNMENT DRAWINGS, SPECIFICATIONS, OR OTHER DATA INCLUDED IN THIS DOCUMENT FOR ANY PURPOSE OTHER THAN GOVERNMENT PROCUREMENT DOES NOT IN ANY WAY OBLIGATE THE US GOVERNMENT. THE FACT THAT THE GOVERNMENT FORMULATED OR SUPPLIED THE DRAWINGS, SPECIFICATIONS, OR OTHER DATA DOES NOT LICENSE THE HOLDER OR ANY OTHER PERSON OR CORPORATION; OR CONVEY ANY RIGHTS OR PERMISSION TO MANUFACTURE, USE, OR SELL ANY PATENTED INVENTION THAT MAY RELATE TO THEM.

THIS REPORT IS RELEASABLE TO THE NATIONAL TECHNICAL INFORMATION SERVICE 5285 PORT ROYAL RD. SPRINGFIELD VA 22161 TELEPHONE 703 487 4650; 703 4874639 (TDD for the hearing-impaired)
E-MAIL orders@ntis.fedworld.gov WWW http://www.ntis.gov/index.html

AT NTIS, IT WILL BE AVAILABLE TO THE GENERAL PUBLIC, INCLUDING FOREIGN NATIONS.

THIS TECHNICAL REPORT HAS BEEN REVIEWED AND IS APPROVED FOR PUBLICATION.

LINDSEY M. SORENSEN, 2d Lt, USAF Program Manager
MICHAIL J. CALIDONNA, Capt, USAF Acting Chief, Weapons Systems Logistics

DONALD R. HUCKLE, JR., Colonel, USAF Chief, Airbase Technologies Division

Do not return copies of this report unless contractual obligations or notice on a specific document requires its return.
Evaluation of Volatile Organic Compound Emissions from the Preparation and Application of BoeGel-EP II

M.V. Henley – AFRL/MLQL
S.E. Wyatt, B.M. Weber – Applied Research Associates

AFRL/MLQL
139 Barnes Drive, Suite 2
Tyndall AFB, FL 32403-5323

AFRL/MLQL
139 Barnes Drive, Suite 2
Tyndall AFB, FL 32403-5323

Effort to reduce ground-level ozone production resulting from Department of Defense (DoD) operations often involve the substitution of materials with lower volatile organic compound (VOC) concentrations. VOCs are known to react in the atmosphere and lead to the production of ozone, a regulated pollutant. However, the amount of ozone producing varies with each individual VOC and with the concentration of nitric oxides (NOx) present in the airshed. To better assess the air quality impact of a VOC, it is necessary to know its atmospheric chemistry mechanisms. That is to say, what are its kinetic rate constants with reactive species in the atmosphere and what are its transformation pathways? Transformation pathways are important since products of reactions may also contribute to ozone production.

A thorough characterization of a formulation’s emission profile coupled with VOC ozone-forming potential (incremental reactivity) provides a means of assessing the product's air-quality impact. This report characterizes the VOC emissions from the preparation (mixing) and application of a sol-gel surface preparation formulation obtained from The Boeing Company and designated as Boe-Gel-EP II.
Evaluation of Volatile Organic Compound Emissions from the Preparation and Application of BoeGel-EP II

M.V. Henley, AFRL/MLQL

Introduction

Efforts to reduce ground-level ozone production resulting from Department of Defense (DoD) operations often involve the substitution of materials with lower volatile organic compound (VOC) concentrations. VOCs are known to react in the atmosphere and lead to the production of ozone, a regulated pollutant. However, the amount of ozone produced varies with each individual VOC and with the concentration of nitric oxides (NOx) present in the airshed. To better assess the air quality impact of a VOC, it is necessary to know its atmospheric chemistry mechanisms. That is to say, what are its kinetic rate constants with reactive species in the atmosphere and what are its transformation pathways? Transformation pathways are important since products of reaction may also contribute to ozone production.

To be able to evaluate and compare the ozone producing potential of various formulations such as fuels, paints and coatings, solvents, etc., the California Resources Board (CARB) adopted a model developed by Carter. The model uses the concept of incremental reactivity to put formulations on somewhat of an equal ground. While not a perfect model it has become an acceptable tool for evaluations. Carter incorporates the atmospheric chemistry mechanisms of 119 VOCs into the model and calculates for these 119 different base case scenarios the average amount of ozone produced when a small amount of VOC is emitted. This average is a single number called incremental reactivity.

The maximum incremental reactivity (MIRvoc) was used as the metric and was derived by Carter by adjusting (mathematically) the NOx concentration and hence the VOC: NOx ratio, in each base case to yield the highest incremental reactivity. MIRvoc calculations were used to derive the ozone-forming potential of the formulation (MIRform) investigated in this study.

A thorough characterization of a formulation’s emission profile coupled with VOC ozone-forming potential (incremental reactivity) provides a means of assessing the product’s air-quality impact. This report characterizes the VOC emissions from the preparation (mixing) and application of a sol-gel surface preparation formulation obtained from The Boeing Co. and designated as BoeGel-EP II.

Methodology

A sample (10 gm or 3 gm) of the mixed coating system was placed inside an evacuable, Teflon coated chamber with an internal volume of 188 liters. Samples of the emitted gases were withdrawn through a side port into a 1/8-in Teflon transfer line routed to a cryogenic sample loop. A vacuum pump/electronic flow controller system maintained a 25 ml/min flow of sample through the cryogenic sample loop. In all cases 100-ml samples were collected. The collection sample loop (1.3 ml-silanized, glass bead filled-trap) was maintained at -65°C and flash heated to 300°C for injection into the gas chromatograph (GC) via a heated rotary valve. Compound separation was achieved using a Restek Rtx-1 column (30m, 0.53mm id., 1.0um film thickness) in a Hewlett-Packard (HP) 5980 II GC equipped with a HP 5972 mass selective detector (MSD).
Helium (UHP, Air Products) was used as the carrier gas. The oven program was a temperature ramp starting at 35°C (hold 5 min.) to 250°C at a rate of 8°C per min. The MSD scanned the effluent from 33 to 350 m/z at a rate of 1.9 scans per second.

The emission profile of the coating system was monitored over a two to five hour period, with samples taken every 30-min. (approx.). The emission time profile of the emitted individual chemicals was determined and used to calculate the individual chemical emission rate. In addition, qualitative headspace/GC/MSD determinations were made on each of the coating systems individual components using solid phase micro extraction (SPME) fibers (carboxen/polydimethylsiloxane).

Mass spectra of the individual emitted chemicals were identified using NIST library comparisons. Quantitation was performed by peak area count comparisons with standard curves prepared from pure known compounds using the described sampling methodology.

Propanol (99.5 %) was obtained from Sigma-Aldrich, and propyl acetate (99%) was obtained from Ultra Scientific. Each BoeGel evaluation kit obtained from Boeing is composed of the following:

Instructions titled “SOL-GEL Kit Procedure”
One 1.0 ml syringe labeled “B1” containing 0.4 ml of acetic acid, glacial.
One 1.0 ml syringe labeled “B2” containing 0.95 ml of zirconium N-propoxide, (23-28% Free Alcohol)
One 2.5 ml syringe labeled “A1” containing 2.0 ml of glycidoxypropyltrimethoxysilane
One 125 ml Nalgene jar labeled “A” containing 100 ml of deionized water
One small container labeled “B” for mixing the “B” series chemicals

Results

The individual compounds identified from emissions of the sol-gel components by headspace SPME analysis are shown in Table 1. Headspace SPME analyses of individual parts and of the Reaction of mix B1 + B2 are qualitatively only. Quantitation was performed on the emission system resulting from the final formulation, i.e. “B1 + B2 + A1 + H2O”.

Table 1. Identification of VOCs in Headspace Samples

<table>
<thead>
<tr>
<th>Component:</th>
<th>Compound(s):</th>
</tr>
</thead>
<tbody>
<tr>
<td>Syringe labeled “B1”</td>
<td>acetic acid</td>
</tr>
<tr>
<td>Syringe labeled “B2”</td>
<td>1-propanol</td>
</tr>
<tr>
<td>Syringe labeled “A1”</td>
<td>glycidoxypropyltrimethoxysilane</td>
</tr>
<tr>
<td>Reaction mix “B1 + B2”</td>
<td>acetic acid, 1-propanol, propyl acetate</td>
</tr>
<tr>
<td>Reaction Mix “B1 + B2 + A1 + H2O”</td>
<td>1-propanol, propyl acetate and others above in trace amounts</td>
</tr>
</tbody>
</table>

The emission profile results of BoeGel-EP II are tabulated in Table 2. These results are averaged from three replicate experiments. The only additional compound or reaction product detected by headspace SPME in the final formulation that was not identified in the headspace of the individual components was propyl acetate. The MIR_{voc} for 1-propanol was determined by Carter. The MIR_{voc} for propyl acetate was estimated based on values reported for ethyl acetate and butyl acetate.
Table 2. Emissions of BoeGel-EP II

<table>
<thead>
<tr>
<th>Compound</th>
<th>Rate of Emission (g/min)</th>
<th>Amount of VOC Emitted (ppm)</th>
<th>g VOC/g Form</th>
<th>MIR VOC</th>
<th>AvoC a</th>
<th>Percent of MIR b</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-propanol</td>
<td>1.1 x 10^{-4}</td>
<td>76.90</td>
<td>3.5 x 10^{-3}</td>
<td>2.3</td>
<td>8.3 x 10^{-3}</td>
<td>99.7</td>
</tr>
<tr>
<td>propyl acetate</td>
<td>0.9 x 10^{-3}</td>
<td>5.70</td>
<td>4.5 x 10^{-5}</td>
<td>0.5</td>
<td>2.3 x 10^{-5}</td>
<td>00.3</td>
</tr>
</tbody>
</table>

a $A_{VOC} = MIR_{VOC} \text{ (units of gram O}_3/\text{gram VOC)} \times \text{ Concentration VOC (g VOC/g formulation)}$

b $MIR_{formulation} = \sum_{\text{VOC's in formulation}} A_{VOC} \text{ (units of g O}_3/\text{g formulation)}$

**Discussion**

To give some relative idea of the ozone-forming potential of various formulation systems, the MIR$_{form}$ of BoeGel-EP II is compared, in Table 3, to two coating formulations previously studied by this laboratory. One coating was the currently used coating system (MIL-C-46168 Type IV military specification) and the other was a “low VOC” alternative (WR-CARC) under investigation. Since the sol-gel formulation studied here is intended to replace an acid-based etching formulation containing no VOCs a direct comparison between the two competing technologies was not appropriate.

Table 3. Comparison of Formulations

<table>
<thead>
<tr>
<th>Formulation</th>
<th>MIR$_{formulation}$</th>
<th>VOC$_{Total \text{ Emitted}}$ (g VOC/g formulation)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BoeGel-EP II</td>
<td>0.0083</td>
<td>0.0035</td>
</tr>
<tr>
<td>WR-CARC</td>
<td>0.02</td>
<td>0.03</td>
</tr>
<tr>
<td>MIL-C-46168 Type IV</td>
<td>0.2</td>
<td>0.11</td>
</tr>
</tbody>
</table>

**Conclusions**

The sol-gel formulation investigated is a low VOC, low ozone-forming formulation. The potential exists for release of other VOCs during preliminary mixing steps, particularly acetic acid. However, these emissions are expected to be quite low and insignificant. This formulation shows promise for minimal impact on air quality.

**References**


