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Determination of Fuel Tank Topcoat Material Compatibility

With Diethylene Glycol Monomethyl Ether and

Triethylene Glycol Monomethyl Ether

Thesis

Submitted to

The School of Engineering of the

UNIVERSITY OF DAYTON

In Partial Fulfillment of the Requirements for

The Degree

Master of Science in Chemical Engineering

by

Ryan Kenton Adams

UNIVERSITY OF DAYTON

Dayton, Ohio

May, 2009

DETERMINATION OF FUEL TANK TOPCOAT MATERIAL COMPATIBILITY WITH
DIETHYLENE GLYCOL MONOMETHYL ETHER AND TRIETHYLENE GLYCOL
MONOMETHYL ETHER

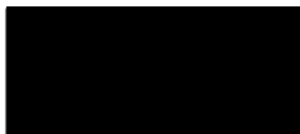
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ABSTRACT

DETERMINATION OF FUEL TANK TOPCOAT MATERIAL COMPATIBILITY WITH DIETHYLENE GLYCOL MONOMETHYL ETHER AND TRIETHYLENE GLYCOL MONOMETHYL ETHER

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University of Dayton, 2009

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This investigation of the conditions which promote fuel tank topcoat peeling (FTTP) in aircraft was performed to assess the requisite conditions for this phenomenon to occur and to determine the feasibility of replacing the current fuel system icing inhibitor (FSII) additive to further prevent such failures. High concentrations of diethylene glycol monomethyl ether (DiEGME), the current FSII, in aqueous and fuel solutions have been shown to cause swelling and blistering of the protective organic coating Boeing Materials Specification (BMS) 10-39 in B-52 aircraft fuel tanks. This can result in a loss of adhesion to the substrate and expose aluminum to corrosion from the bulk fuel. The mechanism for failure is hypothesized to be a result of DiEGME selectively vaporizing from the fuel and then condensing on the coated fuel tank walls at high concentrations. Triethylene glycol monomethyl ether (TriEGME) has been proposed to replace DiEGME as it has a vapor pressure (<0.01 mm Hg @ 20°C) an order of magnitude lower than DiEGME (0.19 mm Hg @ 20°C) and will not volatilize in the headspace of the fuel tank as readily from the bulk fuel. This lower vapor pressure would prevent a high concentration of FSII vapor from forming, which could potentially

condense on the topcoat surfaces and swell the coating. A comparison of the material compatibility of the two additives with the protective topcoat layer was established based upon the absorption and desorption of FSII into or out of BMS 10-39, the hardness of the coating after exposure, and a simulated fuel tank to analyze all aspects of FTTP. These studies will serve to evaluate the differences between DiEGME and TriEGME on topcoat compatibility, determine the requisite conditions for failure, and correlate the FSII concentration in fuel or fuel condensate with a metric for failure.

DiEGME and TriEGME were shown to absorb into the BMS 10-39 layer at equivalent rates and achieve similar final uptake levels for all tested concentrations and solutions. However, TriEGME did not desorb from the topcoat as readily, and required a longer duration to achieve the same reduced concentration levels as DiEGME in the topcoat. The pencil hardness of BMS 10-39 panels after exposure to various concentrations of DiEGME and TriEGME yielded nearly identical results. DiEGME and TriEGME were fully evaluated for their ability to promote FTTP while using the simulated fuel tank, which included the vaporization and condensation processes onto a BMS 10-39 panel above the fuel level. Three possible regimes for FTTP were present for varying concentrations of DiEGME initially in the fuel. Low concentrations (<0.05 vol.%) caused no change in the hardness or color of the panel. As the concentration of DiEGME initially in the fuel increased, the hardness of the BMS 10-39 panel began to decrease rapidly in this transitional range ($0.05 - 0.10$ vol.%). Once a critical concentration (>1.0 vol.%) was reached, the topcoat panel showed visible signs of swelling and blistering as well as a loss of adhesion to the aluminum substrate. TriEGME did not show signs of degradation of the BMS 10-39 panel under any of the tested concentrations in the fuel. The lower vapor pressure of TriEGME relative to the bulk fuel components was able to suppress the selective volatilization from the bulk fuel, and reduce the concentration in the condensate in contact with the topcoat.

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TABLE OF CONTENTS

ABSTRACT.....	iii
ACKNOWLEDGEMENTS.....	v
LIST OF FIGURES.....	viii
LIST OF TABLES.....	xi
LIST OF SYMBOLS AND ABBREVIATIONS.....	xii
CHAPTER	
I. INTRODUCTION.....	1
BACKGROUND.....	1
ORGANIC COATINGS AND BMS 10-39.....	8
RELATED FUEL TANK TOPCOAT PEELING (FTTP) RESEARCH.....	11
EXPERIMENTAL GOALS.....	20
II. EXPERIMENTAL.....	22
BACKGROUND.....	22
BMS 10-39 PANELS USED IN EXPERIMENTATION.....	22
FSII EXPOSURE SOLUTIONS.....	23
FSII ABSORPTION STUDY.....	24
PENCIL HARDNESS STUDY.....	27
INFRARED SPECTROSCOPY STUDY.....	30
FUEL TANK TOPCOAT PEELING (FTTP) SIMULATION STUDY.....	32
ANALYTICAL TECHNIQUES USED IN QUANTIFICATION.....	34
QUANTIFICATION OF FSII IN AQUEOUS MIXTURES.....	34
QUANTIFICATION OF FSII IN ACETONE MIXTURES.....	35
QUANTIFICATION OF FSII IN FUEL MIXTURES.....	36
III. RESULTS AND DISCUSSION.....	38
FSII FUEL ABSORPTION RESULTS.....	38
FSII AQUEOUS ABSORPTION RESULTS.....	42
IR SPECTROSCOPY RESULTS.....	47
PENCIL HARDNESS STUDY RESULTS.....	51

FUEL TANK TOPCOAT PEELING (FTTP) SIMULATION RESULTS.....	61
IV. CONCLUSIONS AND FUTURE WORK.....	75
CONCLUSIONS.....	75
FUTURE WORK.....	77
BIBLIOGRAPHY.....	79

LIST OF FIGURES

Figure 1: Diethylene glycol monomethyl ether (DiEGME) chemical structure.....	2
Figure 2: Fuel tank topcoat peeling (FTTP) occurring in a B-52 wing fuel tank (Aliband et al. 2006).....	3
Figure 3: Clogged B-52 boost pump intake (4-mesh) with BMS 10-39 flakes (Augostini, 2003).....	4
Figure 4: FTTP phenomenon instigated by a DiEGME rich ullage vapor and condensation on the topcoat surface.....	5
Figure 5: Blisters and swelling in a BMS 10-39 panel after exposure to high concentrations of DiEGME in fuel.....	11
Figure 6: Condensate concentrations of DiEGME after distillation of Jet A-1.....	12
Figure 7: The Equilibrium Solvent Uptake (ESU) of BMS 10-39 after exposure to jet fuels with various levels of DiEGME (Aliband et al. 2006).....	14
Figure 8: The Equilibrium Solvent Uptake (ESU) of BMS 10-39 after exposure to aqueous solutions with DiEGME (Aliband et al. 2006).....	14
Figure 9: Experimental setup for the condensation box used to collect DiEGME and TriEGME vapor condensate samples (Zabarnick et al., 2007).....	16
Figure 10: Comparison of the condensate concentration of DiEGME and TriEGME as a function of the fuel percent distilled (Zabarnick et al., 2007).....	17
Figure 11: BMS 10-39 panels after exposure to 80 vol.% DiEGME and TriEGME aqueous solutions (Hufnagle, 2008).....	18
Figure 12: Pencil hardness of BMS 10-39 panels after exposure to varying concentrations of DiEGME and TriEGME (Hufnagle, 2008).....	19
Figure 13: A BMS 10-39 panel submerged in a 20 mL solution containing FSII within a 30 mL vial.....	24
Figure 14: FSII uptake in new BMS 10-39 panels as a function of time with a 50% FSII/water solution.....	26

Figure 15: Pencil Hardness lead grades used for the study with the acceptable range for BMS 10-39.....	28
Figure 16: A BMS 10-39 after exposure to FSII and subsequent pencil hardness evaluation.....	28
Figure 17: Two BMS10-39 panels submerged in a FSII solution for pencil hardness testing.....	29
Figure 18: ATR-IR spectra of BMS10-39 before and after exposure to pure DiEGME. Peaks indicative of FSII have been identified.....	31
Figure 19: The FSII simulation box apparatus.....	33
Figure 20: Refractive index calibration for DiEGME and TriEGME in aqueous solutions using a Reichart AR200 Digital Refractometer.....	35
Figure 21: Calibration curves for DiEGME and TriEGME concentration in acetone mixtures.....	36
Figure 22: The equilibrium uptake of new panels exposed to DiEGME and TriEGME in Jet A-1.....	39
Figure 23: The uptake of DiEGME and TriEGME in Jet A-1 obtained by old panels that were in service for 40+ years.....	40
Figure 24: The uptake of DiEGME and TriEGME with new and old panels in aqueous solutions.....	43
Figure 25: The uptake of DiEGME in aqueous solutions after a given period of drying time with new panels.....	45
Figure 26: The uptake of TriEGME in aqueous solutions after a given period of drying time with new panels.....	46
Figure 27: IR spectrum of a new BMS 10-39 panel exposed to pure DiEGME as a function of time.....	48
Figure 28: IR spectrum of a new BMS 10-39 panel exposed to pure TriEGME as a function of time.....	50
Figure 29: New panel uptake and wet pencil hardness in a fuel condensate surrogate.....	52
Figure 30: Comparison of the uptake and pencil hardness of new panels after exposure to Jet A-1 and surrogate solutions with varying DiEGME concentrations.....	54
Figure 31: The uptake and pencil hardness of DiEGME and TriEGME in a surrogate with old panels.....	55

Figure 32: Pencil hardness for new panels in surrogate after two hours and "wet" uptake data.....	57
Figure 33: Pencil hardness and equilibrium FSII uptake of new panels in aqueous solutions with varying concentrations of FSII.....	58
Figure 34: Pencil hardness of older panels after being exposed to varying initial FSII concentrations in the bulk fuel.....	63
Figure 35: Old panel exposed to approximately 0.05 vol.% DiEGME initially in the bulk fuel.....	64
Figure 36: Old BMS 10-39 panel exposed to approximately 0.08 vol.% DiEGME initially in the fuel and the pencil hardness measurements.....	65
Figure 37: Old Panel exposed to 0.10 vol.% DiEGME initially in the bulk fuel.....	66
Figure 38: Old panel exposed to 0.10 vol.% TriEGME initially in the bulk fuel.....	67
Figure 39: BMS 10-39 panel in the FTTP simulation box showing severe swelling after one day of exposure to approximately 0.10 vol.% DiEGME in the fuel.....	69

LIST OF TABLES

Table 1: Selected Properties of DiEGME and TriEGME.....	8
Table 2: DiEGME and TriEGME experimental runs with the environmental chamber at 60°C and the condensation surface at 20°C.....	62
Table 3: Multiple DiEGME runs at various temperatures and concentrations (* denotes 2 nd aqueous phase concentration).....	71

LIST OF SYMBOLS AND ABBREVIATIONS

AFRL	Air Force Research Laboratories
ATR-IR	Attenuated Total Reflectance Infrared
CTIO	Coating Technology Integration Office
DiEGME	Diethylene glycol monomethyl ether
FID	Flame Ionization Detector
GC	Gas Chromatography
mL	Milliliter
milliM	Millimolar
MS	Mass Spectrometry
SIM	Selective Ion Mode
TriEGME	Triethylene glycol monomethyl ether
vol.%	Percent by Volume

CHAPTER I

INTRODUCTION

Background

Fuels used in modern military aircraft engines play a vital role in maximizing the overall efficiency of the airplane. Many years of research and development were necessary to determine what properties would prove the most valuable for aviation. This research eventually led to kerosene-based fuels to provide the propulsion for jet aircraft. While these jet fuels proved very effective, they lacked certain properties that could not be economically obtained by further altering the bulk fuel. Because of this, chemical additives were developed and dosed into the bulk fuel to provide the desired functionality. These additives offer a wide range of properties, including, but not limited to corrosion protection, static dissipation, icing inhibition, and thermal stability. Additives are important as they can enhance the initial fuel chemistry at a relatively low cost compared to the bulk fuel.

When an aircraft approaches high altitudes, the exterior of the aircraft is subjected to cold temperatures due to the surrounding environment. While the jet fuel itself has a low freezing point ($< -47^{\circ}\text{C}$), any free water within the fuel will begin to freeze at high altitudes. To remedy this situation, a fuel system icing inhibitor (FSII) was developed and introduced as an additive to selectively partition into any free water present and suppress the freezing point of the aqueous mixture. This additive became required in 1961 when a B-52 Stratofortress crashed, which was attributed to ice

formation blocking the fuel lines to the engines (Langer, 1960). Initially, ethylene glycol monomethyl ether (EGME) functioned as the FSII additive while JP-4 was used by the United States Air Force (USAF). However, EGME was subsequently shown to have a relatively high toxicity and problems arose with volatility in JP-5, the fuel used by the Navy, as EGME reduced the flashpoint below the minimum requirement (60°C) (Martel, 1987). Diethylene glycol monomethyl ether (DiEGME) was found to be an adequate FSII alternative, and transition to this compound began in 1987 for JP-5, and was authorized for use in JP-8 in 1992. DiEGME is currently required in both JP-5 and JP-8 fuels, with a required procurement dosage of 0.10 – 0.15 vol.% for both fuels. The use limits are currently 0.03 vol.% (JP-5) and 0.07 vol.% (JP-8), respective. Figure 1 shows the chemical formula of DiEGME.

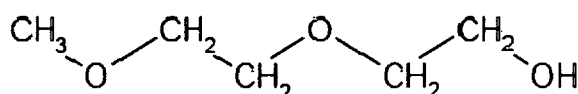


Figure 1: Diethylene glycol monomethyl ether (DiEGME) chemical structure

Some problems have arisen that have been attributed to DiEGME. Within the fuel tanks of some B-52 aircraft, a layer of protective topcoat has begun to peel in a process termed fuel tank topcoat peeling (FTTP) (Aliband et al., 2006; Spicer, 2007; Aliband et al., 2008). This topcoat layer is Boeing Material Specification (BMS) 10-39, and serves as a physical impedance from the fuel coming in contact with the aluminum substrate. A number of consequences are possible as this topcoat layer deteriorates. FTTP allows for corrosion and pitting to occur on the aluminum substrate caused by reactions with the jet fuel. Also, the topcoat flakes that have lost adhesion to the fuel tank walls are left free-floating in the bulk fuel. These flakes can cause problems as they are pumped through the engines along with the fuel. Possible blockages could occur in the fuel filters and valves resulting in a catastrophic failure of the aircraft. Figure 2

shows FTTP inside a B-52 fuel tank exposing the aluminum substrate and Figure 3 shows a boost pump intake screen plugged with BMS 10-39 flakes.



Figure 2: Fuel Tank Topcoat Peeling occurring in a B-52 wing fuel tank (Aliband et al., 2006)



Figure 3: Clogged B-52 boost pump intake (4-mesh) with BMS 10-39 flakes (Augostini, 2003)

BMS 10-39 was formulated for interactions with jet fuel and not to degrade from prolonged exposure. Despite this design, FTTP has occurred while FSII was present in the fuel, and high concentrations of DiEGME in fuel or water have been shown to promote swelling and peeling of the topcoat layer (Aliband et al., 2006; Aliband et al., 2008). FTTP has primarily occurred in two areas within these fuel tanks. These areas are the walls in the headspace of the fuel tank (ullage) and in submerged fuel layers at the bottom of the tank. Each of the areas where peeling has occurred has its own hypothesized mechanism for deterioration. One such hypothesis for FTTP occurring above the fuel level is the concentration of DiEGME is able to increase in the vapor phase as a result of DiEGME having a higher vapor pressure relative to many of the compounds found in JP-8 (Aliband et al., 2006). This DiEGME rich vapor phase then has the potential to condense on the topcoat surfaces if there is a sufficient temperature difference between the vapor and wall resulting in a condensate with a DiEGME concentration which is much higher than the base fuel. The temperature difference is a

result of warm bulk fuel and vapor with a cold fuel tank wall. Figure 4 summarizes this process.

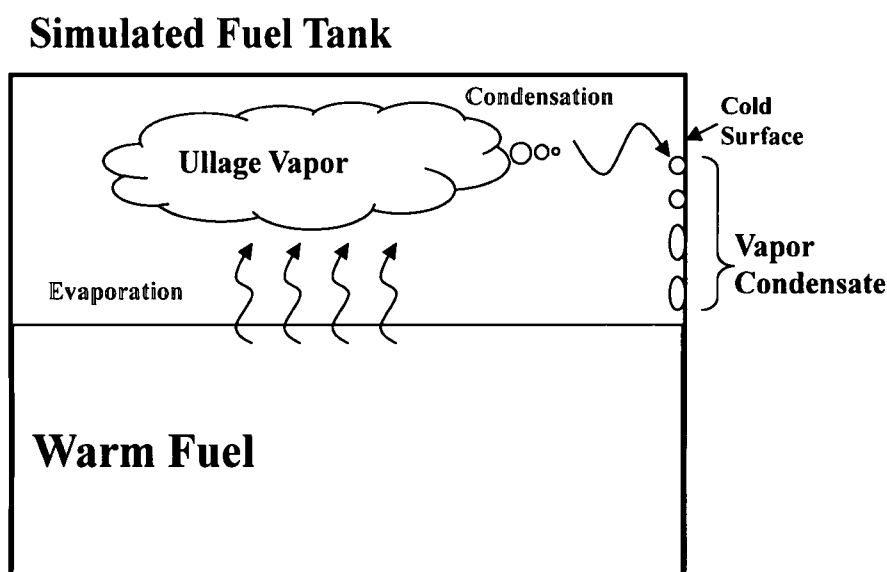


Figure 4: FTTP phenomenon instigated by a DiEGME rich ullage vapor and condensation on the topcoat surface

These conditions of warm bulk fuel and a colder wall temperature to promote selective condensation are possible under specific scenarios. One such possibility for creating the required conditions for FTTP is during takeoff. The fuel tank walls will cool down quickly due to the lower outside air temperature, while the bulk fuel having a larger thermal mass will maintain its heat for a longer period of time. While the timeframe for this phenomenon is small, due to the fuel cooling and reducing the vaporization rate, these conditions will be repeated for continued exposure of DiEGME rich condensate in contact with the topcoat. Another possible scenario involves B-52 aircraft on the ground in warm climates. If the aircraft is left exposed to the sun and thermal radiation throughout a hot day, the bulk fuel in the aircraft fuel tanks can be heated to high temperatures. Similar refueling tanker trucks showed fuel temperatures above 55°C (131°F) during the middle of the day (Williams, 2005). As the sun sets, the temperatures

will decrease quickly. Similarly to the previous scenario, the wall temperatures will cool more quickly due to the differences in thermal mass and provide a cold wall temperature in the ullage for condensation. These conditions may be repeated every day, assuming the weather is warm enough to further vaporize the DiEGME from the bulk fuel.

The second observed location for FTTP in submerged fuel areas is likely initiated by high concentrations of DiEGME in water bottoms. The specific gravity of water and DiEGME (1.00 and 1.02, respectively) are higher than JP-8 (0.8), thus any free water will phase separate and concentrate at the bottom of the tank. DiEGME and water are completely miscible, and DiEGME typically concentrates in water to approximately 50 vol.% within the fuel tank. Higher concentrations of DiEGME in aqueous solutions have been shown to cause FTTP at concentrations up to 80 vol.% with seven day exposures (Hufnagle, 2008). Severe swelling of topcoat flakes has also been shown in similar concentrations (Aliband et al., 2006).

The mechanisms for FTTP to occur are still not fully understood. More information needs to be collected pertaining to the required concentrations, temperatures, and time of exposure to induce FTTP. Along with attempting to validate these methods for FTTP, a number of solutions were proposed to prevent future FTTP. A simple solution would be to re-coat the portions of the fuel tank with exposed aluminum substrate with BMS 10-39 again, or a newer organic coating. This would ensure the aluminum is not in contact with the fuel, and provide an adequate resistance to corrosion. However, re-coating is difficult with limited access to the fuel tanks and can be very costly, and it will not prevent further FTTP. To reduce the occurrence of peeling in submerged fuel areas, it has been proposed to sump the water bottoms on a regular basis. This would ensure that aqueous liquid does not accumulate in the fuel tanks and high concentrations of FSII are not in contact with the topcoat for extended periods of time. Another solution is to reduce the concentration of DiEGME in JP-8. If the

concentration level of DiEGME in the fuel is decreased, this could potentially reduce the concentration of DiEGME in the vapor phase which would be subsequently in contact with the topcoat in the ullage. This approach could also limit DiEGME from partitioning into the water at higher concentration that have caused topcoat failure in the lower portions of the fuel tank. Since DiEGME achieves an equilibrium between the fuel and free water phases, reducing the initial concentration in the bulk fuel would similarly reduce the DiEGME that partitions into the free water. However, the DiEGME concentration still needs to be adequate to provide the required anti-icing efficiency. A proper balance needs to be maintained between reducing the occurrence of FTTP and inhibiting icing.

Another approach is to replace DiEGME with an alternative FSII which does not promote FTTP. With the current hypothesized mechanisms for FTTP occurring on the topcoat walls above the fuel level, a suitable replacement would provide similar anti-icing efficiency, but have a lower vapor pressure. Once such chemical that fits these requirements is triethylene glycol monomethyl ether (TriEGME) which has a vapor pressure of <0.01 mmHg @ 20°C , more than order of magnitude lower than DiEGME at 0.19 mmHg @ 20°C (Zabarnick et al., 2007). TriEGME should not volatilize as readily from the bulk fuel, resulting in a lower effective concentration in any condensate in contact with the topcoat surfaces. Table 1 shows the selected property differences between DiEGME and TriEGME.

Table 1: Selected properties of DiEGME and TriEGME

FSII Additive	Vapor Pressure (mmHg @ 20°C)	Density (g/mL @ 20°C)	Molecular weight (g/mol)	Freezing Point (°C)
DiEGME	0.19	1.023	120	-85
TriEGME	<0.01	1.026	164	-47

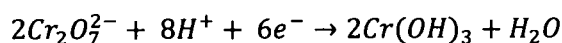
Replacing DiEGME with TriEGME requires an evaluation of material compatibility to ascertain any different interactions with the fuel system components. Further work will also attempt to create an improved understanding of FTTP. This will be carried out by evaluating the effects of FSII concentration in fuel or water on FTTP as well as the feasibility of replacing DiEGME with TriEGME. In addition to this work, a literature review of BMS 10-39 and organic coatings was conducted to provide information pertaining to FTTP and the failure mechanisms.

Organic Coatings and BMS 10-39

Organic coatings, which include BMS 10-39, have desirable properties for uses in corrosion control. Coatings are composed of four categories of components: binders, volatile components (or carrier), pigments, and additives. All four component categories can be altered to provide the requisite properties for the desired application. Binders are the bulk component of the coating, and are generally comprised of a polymer matrix. The binder adheres to the metallic substrate and essentially governs the properties of the coating film. The volatile component, or carrier, is included to enhance the application process of the coating. These are liquids that function by ensuring the coating is fluid enough to be applied to the substrate. After the application of the coating, the carrier will evaporate from the bulk of the polymer, which will begin to harden. Pigments are insoluble particles that can provide color or opaqueness to the

coating. These are generally more important for commercial applications, such as to provide color for paints, though some pigments can affect the application characteristics and film properties. Additives in coatings are very similar to additives in jet fuel. They are small quantities of material that are added to enhance some properties of the coating, such as flow modifiers. (Wicks et al., 1992; Forsgren, 2006)

Organic coatings used for corrosion protection function in one of two methods. They either slow down the corrosion process by creating a physical barrier to the substrate, or by chemically altering the substrate surface to lower the corrosion reaction rate. Coatings, such as BMS 10-39, that inhibit fluid and ion flow have a strong polymer matrix. These types of coatings also serve as a barrier between an anodic and cathodic reaction with the metal substrate (Westing et al., 1993, 1994). Adhesion also plays a very prominent role in corrosion protection. If adhesion is lost between the coating and the substrate, fluid transported through the coating can begin the electrochemical corrosion process. In order for strong adhesive bonding between the coating and the metal surface to occur, cleaning and surface preparation is required to remove any debris or oils. This is then followed by a chemical treatment with a conversion coating which serves as a corrosion inhibitor. For steel, these conversion coatings are phosphate based and the effectiveness is dependent upon the pH of the solution. Aluminum requires a different conversion coating, as the aluminum surface is a thin and dense layer of aluminum oxide. The chemical washes used for providing corrosion protection for aluminum are generally chromate conversions (Westing et al., 1993; Wicks et al., 1994; Sekine, 1998; Forsgren, 2006). Specifically, in the case of fuel tank interiors for B-52, Alodine is used. Alodine is a chemical mixture containing di-chromate oxide ions that undergo the following redox reaction with the aluminum surface (Zhao, 2001):



This layer of chromium hydroxide has shown a very high electrochemical resistance to corrosion. Combined with an epoxy coating, such as BMS 10-39, to impede fluid and ion flow to the aluminum substrate, this provides a strong corrosion resistance.

However, with continuous contact to corrosive elements, the organic coating will lose its resistance to fluid and ion transport as well as its adhesive properties due to increasing voids in the polymer matrix. Swelling or blistering can occur in the polymer matrix as the coating retains larger molecules and ions. Blistering is a function of the osmotic pressure from these contaminants in the coating or high ionic strengths due to the ions formed from the corrosion reaction at the metal surface (Westing et al., 1994; Wicks et al., 1994). Once blisters are formed, they are easily expanded to expose larger areas for continued degradation.

For epoxy coatings, such as BMS 10-39, the loss of adhesion is believed to be preceded by excessive swelling (Westing et al., 1994). This swelling and blistering has been very evident in the fuel tanks in B-52 aircraft. Figure 5 shows an example of cracks and blisters on a small topcoat panel caused from exposure to fuel condensate at 0.25 vol.% DiEGME.

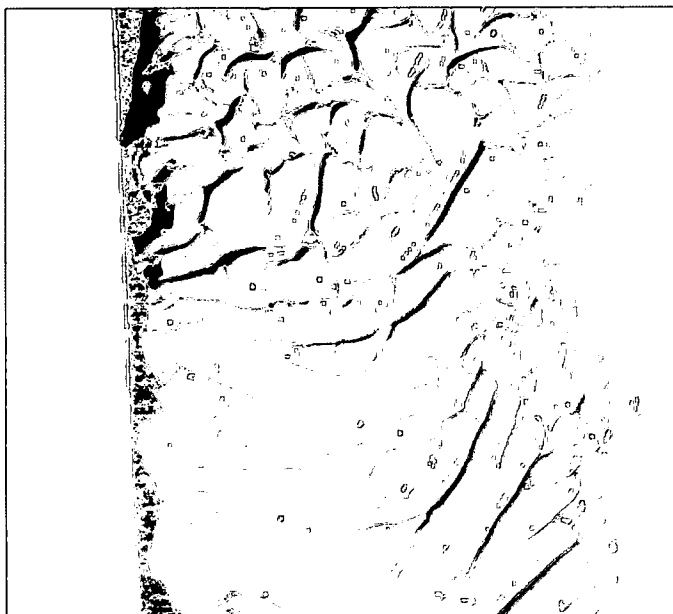


Figure 5: Blisters and swelling in a BMS 10-39 panel after exposure to high concentrations of DiEGME in fuel

The swelling and blistering of BMS 10-39 caused by high concentrations of DiEGME is very severe and can subsequently lead to corrosion of the aluminum substrate. In order to prevent future FTTP occurrences, changes will need to be made to the current concentration of DiEGME in the fuel, or be replaced by TriEGME as the specification FSII. The feasibility of these solutions will be investigated based upon various studies analyzing the FSII and FTTP.

Related Fuel Tank Topcoat Peeling (FTTP) Research

Previous research performed pertaining to FTTP has provided a better understanding of this process, though these studies do not fully explain the phenomenon. Determining the requisite conditions for DiEGME to cause FTTP has been the goal for many research groups. One such study performed in our laboratory involved the distillation of jet fuel for the purpose of analyzing the selective DiEGME volatilization into the vapor headspace. This experiment was performed in a typical glass

distillation apparatus with the condensate collected and analyzed for the DiEGME concentration every 1% distilled. The distillation results using Jet A-1 and various initial DiEGME concentrations are shown in Figure 6.

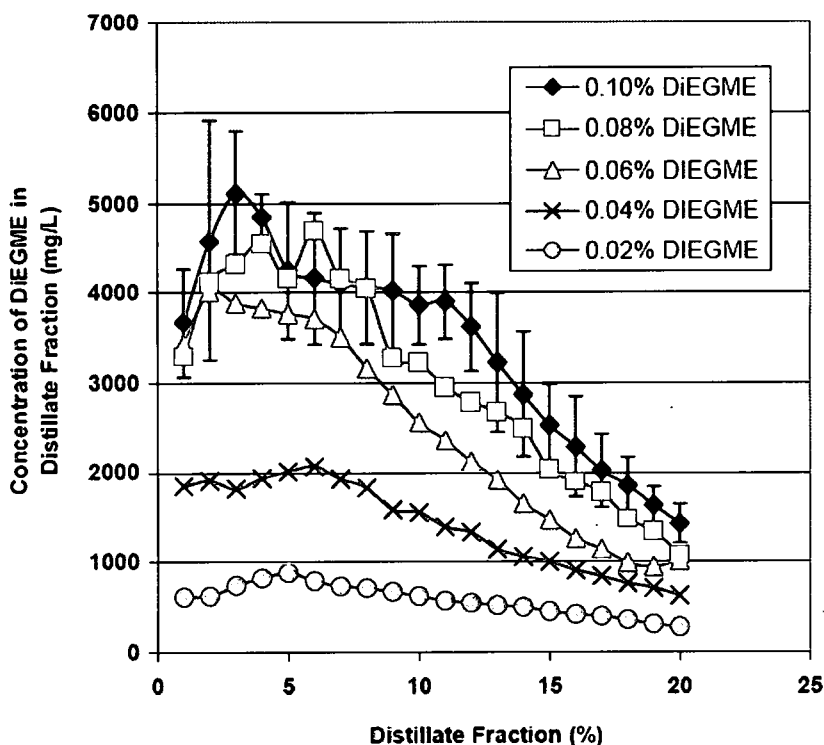


Figure 6: Condensate concentrations of DiEGME during distillation of Jet A-1

The five distillation runs produced very similar trends. With an increasing initial concentration of DiEGME in the fuel, there is a much larger concentration reached in the distillate. The highest concentration of DiEGME in the fuel yields the highest concentration of DiEGME in the condensate. The highest point for each of the runs, representing the largest concentration of DiEGME, is near 5% distilled or lower. After this maximum, the distillate fraction contains decreasing amounts of DiEGME. The concentrations reached in the distillate are also quite high, reaching 0.50% vol.% DiEGME with an initial concentration of 0.10%. This data verifies that DiEGME is volatilized readily and selectively from the bulk fuel relative to the majority of fuel

components, and that the distillate concentration is proportional to the initial concentration in the fuel. Since the concentration of DiEGME in the condensate is proportional to that dosed in the fuel, a lower dose concentration would potentially render a significantly lower concentration in contact with the ullage surfaces. It should be noted this is a "forced" distillation because it was performed at a high temperature, however the components should volatilize in a similar manner at lower temperatures.

The interaction between FSII and BMS 10-39 has also been analyzed to determine the role of DiEGME in deteriorating organic coatings. Aliband et al. (2006) have performed a number of Equilibrium Solvent Uptake (ESU) experiments to investigate BMS 10-39's resistance to swelling by JP-8, JP-4, and aqueous solutions with varying concentrations of DiEGME. The experimental approach involves placing paint fragments of BMS 10-39 topcoat in a given volume of fuel or water with a specific concentration of DiEGME. The weight of the paint chip before and after exposure to jet fuel is recorded and the DiEGME absorption is defined in terms of ESU(%):

$$ESU(\%) = \frac{[Wet\ Weight] - [Dry\ Weight]}{[Wet\ Weight]} \times 100$$

This allows for a direct measurement of how much weight due to absorption of aqueous or fuel components a BMS 10-39 chip has gained after exposure. Figure 7 shows the ESU (%) as a function of DiEGME concentration in both JP-4 and JP-8 while Figure 8 shows the ESU (%) for aqueous solutions.

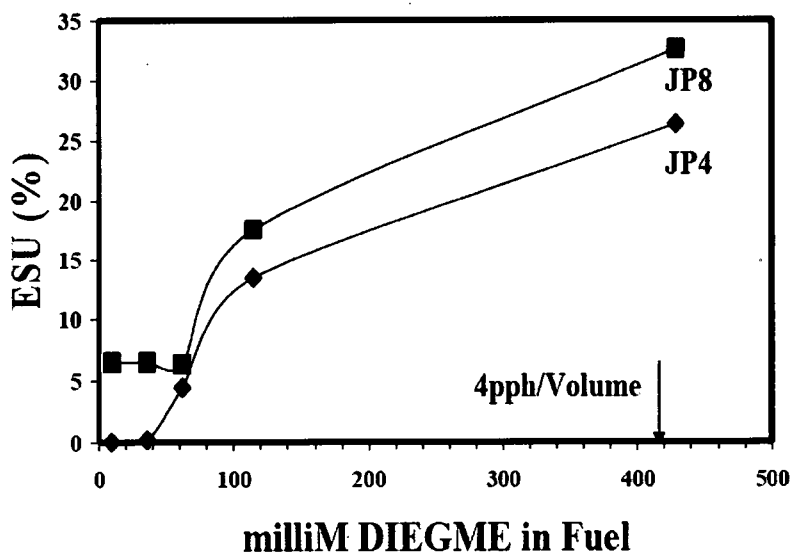


Figure 7: The Equilibrium Solvent Uptake (ESU) of BMS 10-39 after exposure to jet fuels with various levels of DiEGME (Aliband et al., 2006)

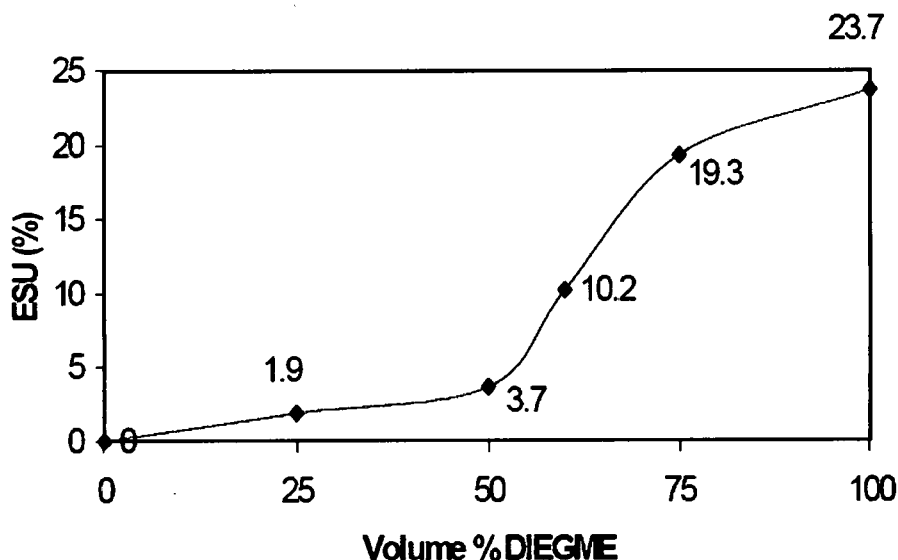


Figure 8: The Equilibrium Solvent Uptake (ESU) of BMS 10-39 after exposure to aqueous solutions with DiEGME (Aliband et al., 2006)

The ESU for JP-8 is initially at 6% and does not change up to approximately 75 milliM DiEGME (0.90 vol.%). At increasing concentrations of DiEGME, the ESU rapidly increases up to 33% ESU. JP-4 shows a similar curve, though BMS 10-39 shows a greater resistance to JP-4 at 50 milliM DiEGME (0.60 vol.%) or less. Both data sets show a strong relationship between BMS 10-39 and the concentration of DiEGME in fuel. Higher concentrations of DiEGME in fuel will yield increased swelling of the topcoat

and ultimately problems with the coating integrity and adhesion. The aqueous data shows a similar trend to the JP-4 and JP-8 data. Initially, there is only a small increase ($< 5\%$ ESU), but with DiEGME concentrations greater than approximately 50 vol.% in the aqueous solutions, the ESU becomes much larger. This increase in ESU suggests a much higher absorption of DiEGME into the topcoat chips once the solution is predominately composed of DiEGME. This could be a result of insufficient total water molecules to "stabilize" DiEGME molecules in the liquid phase. Qualitatively, the BMS 10-39 chips after exposure to concentrations greater than 75 vol.% DiEGME were described as leathery and soft, indicating a weakening of the topcoat. There are some limitations with this fuel data, as it is not possible to selectively determine what components are being absorbed into the topcoat layer for fuel. It also is unable to directly correlate uptake with FFTP. While this study gives some qualitative descriptions of the BMS 10-39 after exposure, it still cannot determine if any degradation has occurred.

The feasibility of employing TriEGME to replace DiEGME is still largely unknown, though some studies were performed to compare their difference in vapor pressures and the effect on volatilization. One such experiment attempted to simulate a small-scale fuel tank and compare the vaporization of DiEGME and TriEGME (Zabarnick et al., 2007). This study was designed to investigate if TriEGME will volatilize into the headspace as readily as DiEGME under similar conditions. The box that acted as a fuel tank was placed in an environmental chamber and heated to 60°C to allow for vaporization of the fuel. Inside the box was a small vacuum-jacketed glass collector that was independently chilled to the desired temperature to promote condensation on this surface. This experimental design facilitated selective condensation into the glass collector. The experimental setup is shown in Figure 9.

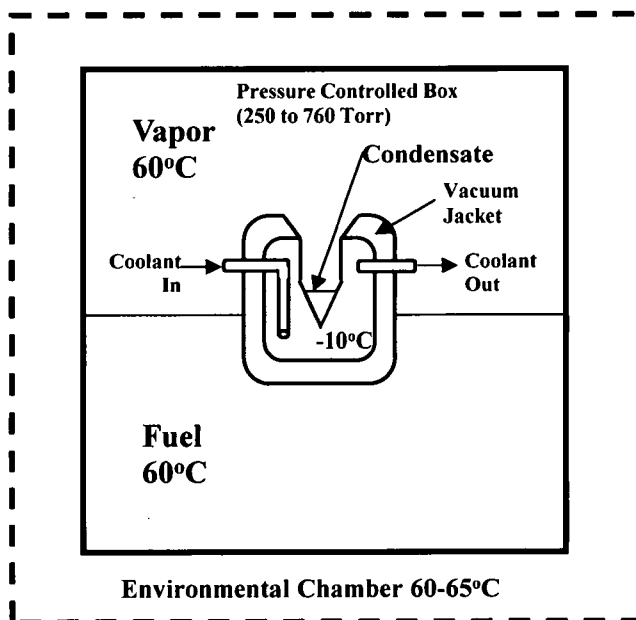


Figure 9: Experimental setup for the condensation box used to collect DiEGME and TriEGME vapor condensate samples (Zabarnick et al., 2007)

The condensate was collected in-situ from the glass condenser as a function of time and analyzed to obtain the concentration of DiEGME or TriEGME. The initial concentration of FSII in the fuel was held constant at 0.14 vol.%, which is close to the current maximum procurement limit in JP-8. Figure 10 shows the results from this experiment.

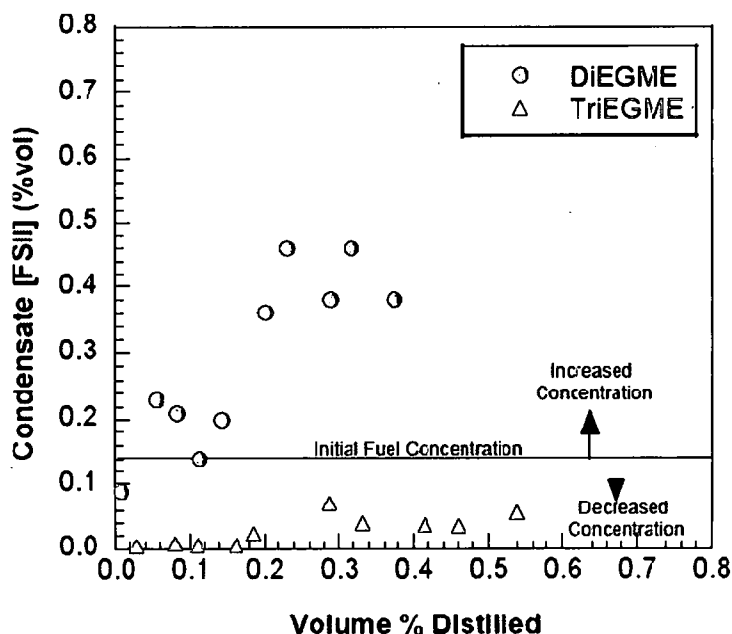


Figure 10: Comparison of the condensate concentration of DiEGME and TriEGME as a function of the fuel percent distilled (Zabarnick et al., 2007)

The DiEGME curve shows a general increase in the concentration in the condensate as the volume percent distilled increases. The TriEGME data, however, differs greatly from the DiEGME data. The TriEGME concentration in the condensate decreases from the initial fuel concentration, and only reaches a maximum of approximately 0.08 vol.%, which is significantly lower than the maximum achieved by DiEGME at approximately 0.50 vol.%. TriEGME, with its lower vapor pressure, seems to prevent high FSII concentrations in the headspace under these conditions. This data demonstrates the potential of a less volatile FSII to reduce the effective concentration in any condensate formed on ullage surfaces.

An additional study was performed to evaluate the material compatibility of DiEGME and TriEGME solutions in contact with BMS 10-39. The Air Force Research Laboratory (AFRL) Coating Technology Integration Office (CTIO) performed adhesion and hardness testing of topcoat panels in contact with fuel and vapor phase FSII solutions (Hufnagle, 2008). This work assessed if any differences are present for the

topcoat degradation process for DiEGME and TriEGME in direct contact with the topcoat. The BMS 10-39 panels, cut into 3" by 6" rectangles, were half submerged in specific concentrations of FSII in water or a fuel surrogate for 7, 14, or 60 days. This fuel surrogate was used to simulate the condensate that would be vaporized from JP-8, which will be further discussed in the experimental section. The concentrations ranged from 0.01 -1.50 vol.% for FSII in a fuel surrogate while the aqueous solutions were concentrated to 80 vol.% FSII at ambient pressure and 60°C. These concentrations for the fuel and aqueous solutions were chosen to match previous FSII compatibility testing conducting at the CTIO, and were believed to represent a very severe exposure regime. For all the experiments, DiEGME and TriEGME performed almost identically. There was a lack of data for aqueous solutions, as the BMS 10-39 completely delaminated from the aluminum substrate. Most of the panels appeared as shown in Figure 11 after exposure.

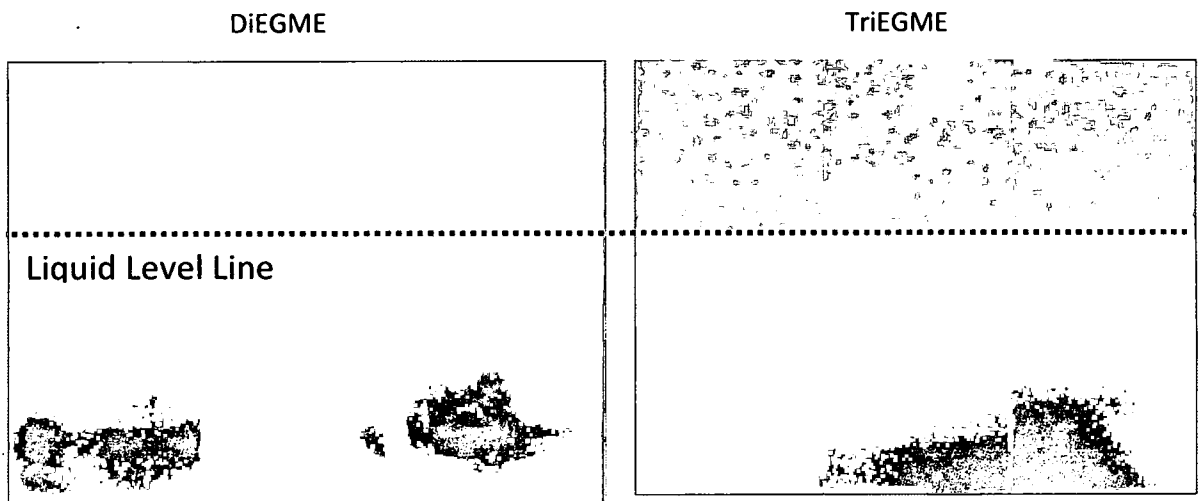


Figure 11: BMS 10-39 panels after exposure to 80 vol.% DiEGME and TriEGME aqueous solutions (Hufnagle, 2008)

The topcoat is completely delaminated from the aluminum substrate after contact with 80 vol.% FSII, both above and below the liquid level line. Pitting and corrosion of

the aluminum occurred above the liquid level, possibly suggesting the corrosion process is promoted in the vapor phase.

The BMS 10-39 panels exposed to the surrogate did not completely delaminate from the aluminum. These panels were analyzed by pencil hardness testing after exposure to FSII to evaluate the degree of degradation. The dose concentrations of DiEGME and TriEGME took into consideration the different vapor pressures of these chemicals. TriEGME had lower concentrations (0 to 0.10 vol.% in the surrogate) since it has been shown to not vaporize as readily, while the DiEGME concentrations were higher (from 0.10 to 1.50 vol.%). The pencil hardness data was collected two hours after removal from the solutions, and is shown in Figure 12.

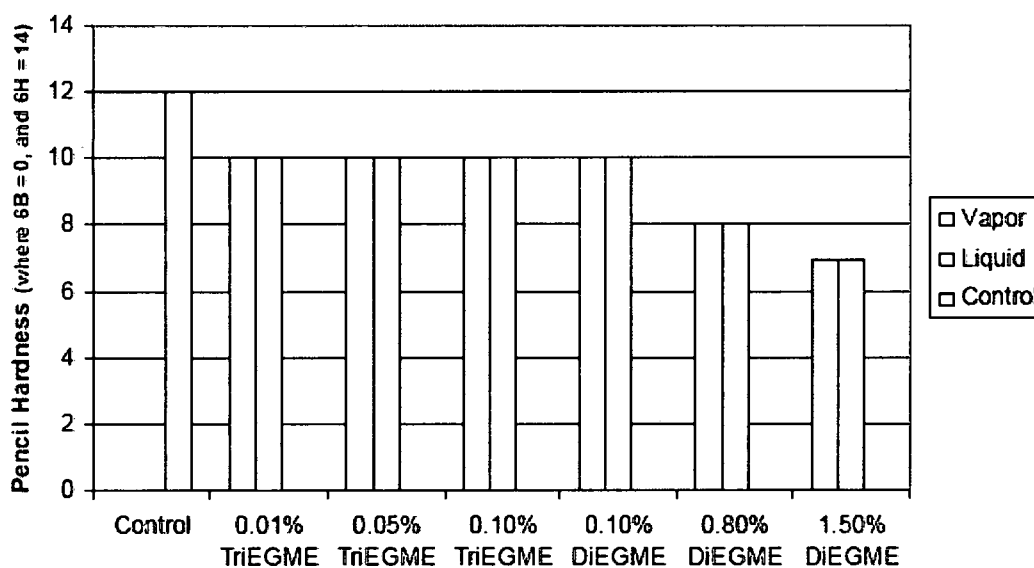


Figure 12: Pencil hardness of BMS 10-39 panels after exposure to varying concentrations of DiEGME and TriEGME (Hufnagle, 2008)

The pencil hardness was rated from 0 to 14 (6B-6H), with 14 being the hardest and 6 being the minimum passing hardness for BMS 10-39 coatings. Further pencil hardness testing will be discussed in the Experimental Section. The hardness of the panels exposed to the liquid versus vapor phases did not differ for any of the concentrations. The control was the rated the hardest at 12, but any contact with FSII in

the surrogate reduced this. TriEGME did not lower the hardness beyond the initial decrease for any of the three concentrations, while DiEGME decreased by a total of 5 hardness ratings from the control at the highest concentration of 1.50 vol.%. There are some limitations to this data, as there are a number of variables that have not yet been investigated. It would be useful to further evaluate the concentrations ranges to determine what concentration of FSII in the fuel or surrogate will cause a failure. This data does at least provide supportive information that higher concentrations of DiEGME in a fuel surrogate can decrease the topcoat integrity. This decrease in hardness could potentially cause swelling and blistering in the topcoat which would lead to FTTP. It would be beneficial to further investigate pencil hardness experiments and the effects of FSII in fuel or water in contact with BMS 10-39.

Overall it has been determined that DiEGME can selectively volatilize from the jet fuel and most likely promotes FTTP in DiEGME rich aqueous and hydrocarbon solutions. TriEGME has shown promise to replace DiEGME as it does not selectively volatilize into the headspace as readily as DiEGME. However, there are still factors which previous research has not fully addressed. The studies outlined in the Experimental Section were designed to address key factors affecting FTTP and provide improved information pertaining to topcoat compatibility and failure occurrences.

Experimental Goals

Based upon the previous research relating to FTTP, further investigation of the requisite conditions for this phenomenon to occur is required. A comparison of DiEGME and TriEGME is also essential to assess TriEGME as an alternative anti-icing inhibitor. Determination of the anti-icing efficiency of TriEGME and DiEGME at lower concentrations is being evaluated in other studies. The experiments in this study were designed to assess the effects of DiEGME and TriEGME using the most probable

scenarios relating to FTTP. The absorption of FSII into BMS 10-39 was quantified to further analyze the effects of concentration in aqueous or fuel solutions and exposure conditions. Along with this quantified absorption information, a metric to correlate the extent of absorption to a failure rating would further provide details on FTTP. These studies investigate any difference between DiEGME and TriEGME using topcoat panels that were recently fabricated and those that were exposed to fuel for many years, as well as the requisite conditions which will reduce the topcoat integrity below the minimum specification requirement. Studies were also performed to preliminarily investigate the desorption rates of FSII from the topcoat. BMS 10-39 has been observed to 're-harden' as a function of time (Aliband et al., 2006), and this phenomenon is most likely due to FSII molecules desorbing from the coating. An ultimate goal is to attempt to reproduce FTTP in a controlled setting. This capability would assess the differences between DiEGME and TriEGME as well as investigate the degradation process of FTTP. These studies will provide a knowledge base for the conditions necessary for FTTP to occur as well as assess the potential FSII alternative, TriEGME.

CHAPTER II

EXPERIMENTAL

Background

The studies used to achieve the experimental goals are described in this section, as well as any pertinent information relating to the analysis of FSII effects on topcoat. The latter information includes background material of BMS 10-39 used for experimentation as well as analytical techniques used for FSII quantification in the topcoat or various solutions.

BMS 10-39 Panels Used in Experimentation

The experimental studies were performed to investigate the compatibility of FSII with both aged and new BMS 10-39 topcoat panels. Both types of panels were evaluated to determine any differences of FTTP between the new and aged panels after exposure to DiEGME and TriEGME. The CTIO office fabricated 1-sided topcoat panels on 1/32 inch aluminum to meet the BMS 10-39 specifications, including a 1 mil thickness. These manufactured panels are referred to as "new" panels, as they have not been exposed to fuel or FSII before these studies. The other BMS 10-39 coatings tested were obtained from a scrapped Model-G B-52 aircraft from Boeing Wichita and had been in contact with JP-4 with EGME or JP-5 with DiEGME. These panels are referred to as "old" panels. The older panels exhibited signs of wear based upon a decreased topcoat thickness (approximately 0.7 mil) and a "chalky" side of the topcoat. This chalky residue

on one the side of the panel was possibly explained by exposure to external weather conditions over a long period of time. The chalky side of BMS 10-39 was eventually removed from the older panels with a razor blade, as experimentation indicated that it is most likely not representative of current topcoat in B-52 aircraft. These "new" and "old" panels were used as described in the experimental studies.

FSII Exposure Solutions

Interactions with the BMS 10-39 topcoat can occur with FSII in various solutions. Three different bulk solutions were used in the experimental studies while varying the FSII concentrations; these include water, fuel, and a surrogate fuel condensate. Aqueous solutions were used for many of the studies to evaluate the required concentrations for FTTP to occur in a water bottom. The water used to create the solutions was purified via reverse osmosis. A clay treated Jet A-1 (POSF 4877) was used as the base fuel in almost all of the experimental studies. Jet A-1 is the unadditized base fuel for JP-8. The clay treatment was necessary to remove any FSII contamination in the Jet A-1 during transportation and storage. Finally, a surrogate was developed to simulate the fuel condensate which would be in contact with the BMS 10-39 coating above the liquid fuel level. This surrogate was comprised of Exxsol D40 (85%), Aromatic 100 (9%), and Aromatic 150 (6%). The mixture accurately represented the lighter components that are initially vaporized from the bulk fuel (Zabarnick et al., 2007). Ideally, this surrogate would provide a more precise simulation of FTTP, as high concentrations of DiEGME have not been found in the fuel, but in the fuel condensate. These three solutions were used throughout the following experimental studies.

FSII Absorption Study

The uptake study investigates the liquid-solid interactions between FSII and the BMS 10-39 layer by quantifying the FSII absorbed into the topcoat through direct contact. This information provides a more complete understanding of the exposure of various FSII concentrations in the condensate or bulk fuel on the topcoat integrity. The experiment was designed to submerge small topcoat panels in fuel and water with specific concentrations of DiEGME and TriEGME, then remove the panels and quantify the mass of FSII absorbed. Small (0.5"x 0.5") aluminum panels were used with BMS 10-39 coating. Both new and old panels were used as discussed previously. These panels were submerged in 20 mL of an aqueous or fuel solution with a known concentration of FSII in a 30 mL vial that was capped during testing. Figure 13 shows the schematic of the typical experimental setup.

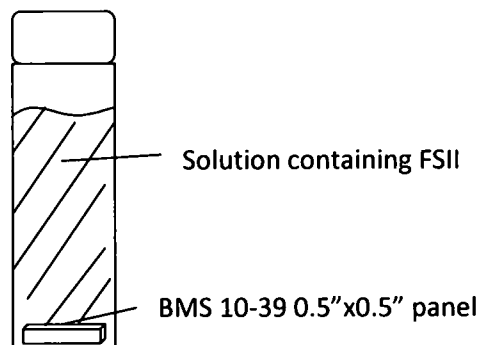


Figure 13: A BMS 10-39 panel submerged in a 20 mL solution containing FSII within a 30 mL vial

This volume of liquid was used to ensure there will not be a significant change in the FSII concentration of the liquid phase due to partitioning into the topcoat. This was verified by analyzing the concentration of the solution before and after exposure to a BMS 10-39 panel; the change in concentration was below measurement sensitivity.

The aqueous solutions ranged from 0-100% of DiEGME or TriEGME, while the fuel or surrogate solutions ranged from 0-2%. This difference in concentration ranges was a result of the typical concentrations expected in the field, as well as to the solubility difference of the FSII, which is fairly polar and has limited solubility in hydrocarbon fuels. The panels were left exposed to the solutions for a specified period of time. Initially, the solutions were placed into a shaker to be agitated throughout the duration of contact; however, further studies revealed that agitation was unnecessary due to the short time required for the FSII in the liquid and topcoat layer to reach equilibrium. The exposure time was five days, as further time did not increase the absorption of FSII in the topcoat. Later, this was shortened based upon the absorption study discussed below. After this equilibrium was achieved, the panels were removed from the vials and cleaned in order to remove any liquid droplets remaining on the panel from solution. This cleaning consisted of rinsing with a small volume of hexane (1-2mL) and then blot drying with Kimwipes such that there were no wet marks on the topcoat. The panel was then submerged in 2mL of acetone for one hour to extract the absorbed FSII component from the topcoat. These panels could subsequently be reused for other uptake studies, as the acetone extraction removes any detectable levels of FSII in the topcoat. This was evident by performing consecutive acetone extractions on the same panel after exposure, with the second extraction resulting in undetectable levels of FSII. The acetone extraction was collected and analyzed to obtain the FSII concentration as well as the total mass absorbed (see Quantification of FSII in Acetone Mixtures). Using the known weight of the topcoat, determined by thickness measurements and the density obtained by weighing a known volume of a topcoat flake, the FSII absorption quantity was normalized by the moles of FSII absorbed per liter of topcoat. Each experimental condition was performed in triplicate to obtain a measure of reproducibility.

This basic approach was modified to investigate the rate at which FSII can be absorbed into the topcoat, as well as the rate at which the desorption of FSII occurs. In order to evaluate the absorption rate, the exposure time of the topcoat in contact with a FSII solution was varied to determine when the uptake concentrations reached a plateau. A plateau of the data suggests that the topcoat no longer absorbs FSII and reached equilibrium with the FSII in the solution. The panels were removed from the solutions at varying times between 10 seconds and 144 hours. This was performed with new panels and 50% aqueous solutions of DiEGME and TriEGME. Each data point represents the average of three uptakes at the specific time. Data from this study is shown in Figure 14.

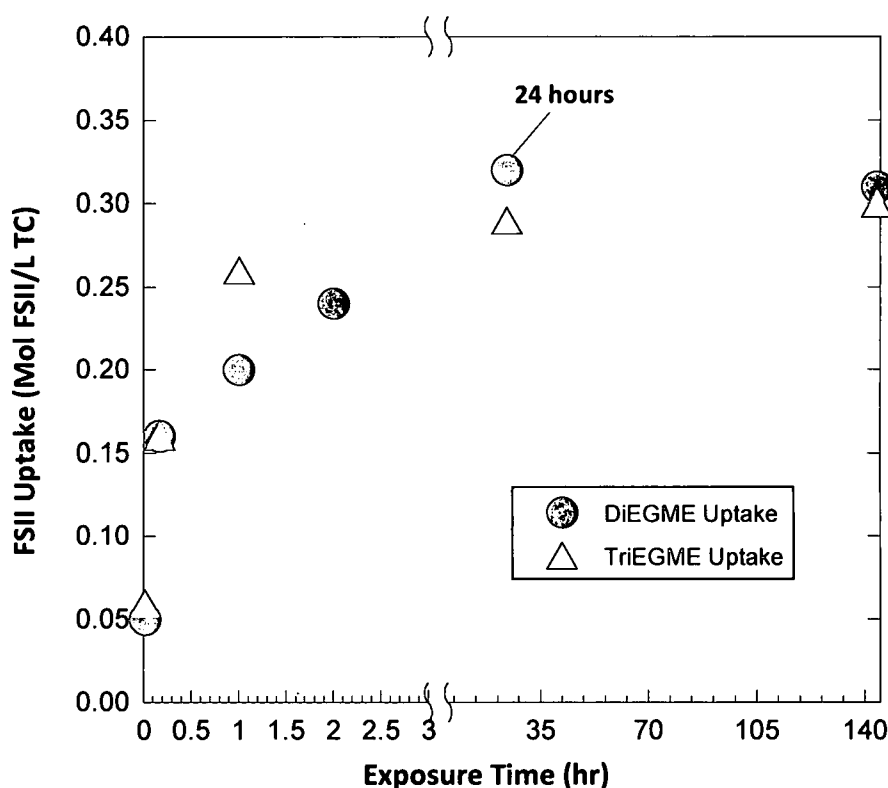


Figure 14: FSII uptake in new BMS 10-39 panels as a function of time with a 50% FSII/water solution

The FSII uptake increases very rapidly for the first two hours of exposure for TriEGME and DiEGME. After 24 hours of topcoat exposure, the uptake no longer increases and is statistically identical to the uptake after five days. Based upon Figure 14, the time to reach equilibrium with FSII in water in contact with BMS 10-39 is between 2 hours and 1 day. This data was used to validate reducing the exposure time for the absorption study to one day for later experiments from the initial five days.

Alternatively, the desorption rate was qualitatively analyzed by varying the time between the cleaning of the panel (after removal from the solution) and the acetone extraction. This additional time allowed for the topcoat to slightly re-harden and for some FSII loss due to evaporation. Equilibrium absorption data as a function of FSII concentration as well as the desorption data as a function of concentration and time is discussed in the absorption study results.

This experimental procedure to quantify the FSII uptake differed from the previous methods used by Aliband et al. (2006). The aforementioned study used topcoat flakes that were not adhered to an aluminum substrate, and the ESU(%) was based solely on the total weight gained from contact with FSII in an aqueous or fuel solution. While this provided a simple and quick method to evaluate the absorption into the topcoat flakes, it was unable to selectively quantify the FSII component in the topcoat. Using the acetone extractions to remove and selectively quantify the FSII absorbed provides a more direct analysis of the FSII uptake

Pencil Hardness Study

While the uptake study provides valuable insight regarding the quantity of FSII absorbed into BMS10-39 topcoat, it does not directly correlate the quantity of FSII absorbed to the integrity or stability of the coating after exposure. In order to evaluate these aspects, pencil hardness testing was performed. This was performed according to

The pencil hardness study was performed on 1" x 2" panels of new and old BMS 10-39 on aluminum. The panel size was chosen to allow for the use of all leads required to determine the hardness. Two such panels were submerged in 100 mL beakers with 80 mL of a FSII solution for two days. This exposure time allowed for two data sets to be collected per week while still maintaining equilibrium with FSII in the fuel or water and the topcoat. Similar to the uptake study, this volume of liquid was used to ensure the concentration of FSII in the solution did not decrease during the duration of exposure. This was verified by analyzing the concentration of DiEGME in a solution before and after exposure which did not significantly change over the two days. The panels were arranged as shown in Figure 17 before covering the beaker to prevent evaporation.



Figure 17: Two BMS10-39 panels submerged in a FSII solution for pencil hardness testing

When the panels were removed, both were washed with a small amount of hexane to remove the remaining solutions droplets on the BMS 10-39 panel. One of the panels was immediately tested for its pencil hardness, while the other was allowed to dry in a fume hood for two hours prior to evaluation. The latter approach was performed to

determine the ability of the topcoat to re-harden and/or re-adhere over time as evaporation of FSII occurs.

Infrared Spectroscopy Study

Further investigation of the desorption rate of FSII from the topcoat was obtained in a non-destructive manner by using Attenuated Total Reflectance Infrared Spectroscopy (ATR-IR). ATR-IR functions by analyzing the chemical makeup of solids or coatings via absorption of energy of specific wavelengths based on the types of bonds. When DiEGME or TriEGME is absorbed into the topcoat, and evaluated via ATR-IR, a large number of peaks are discernable representing the FSII component. These peaks represent IR absorption caused by specific molecular bond types present in DiEGME or TriEGME. Figure 18 is a spectra of a BMS10-39 coated new panel prior to exposure to FSII and after the coating was in contact with pure DiEGME for one day, with the peaks identified by functional group.

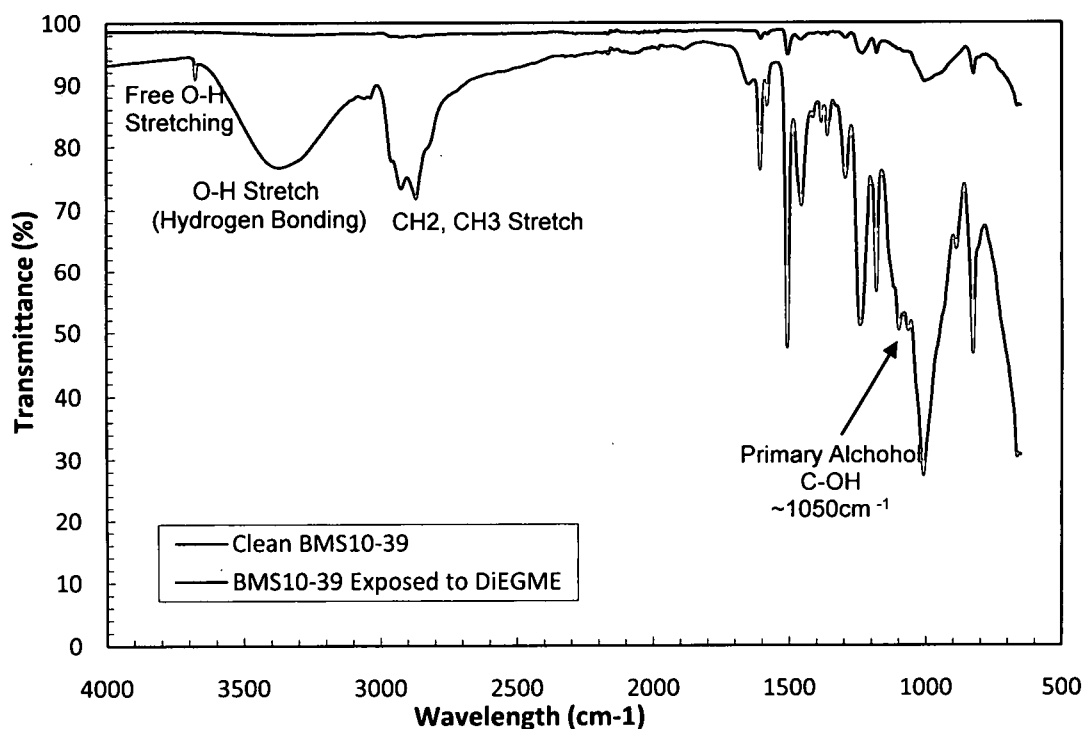


Figure 18: ATR-IR spectra of BMS10-39 before and after exposure to pure DiEGME. Peaks indicative of FSII have been identified

The panel exposed to pure DiEGME shows numerous peaks not present in the original BMS10-39 spectrum. Many peaks are identifiable as bonds or functional groups present in DiEGME and TriEGME. This method is different than the acetone absorption study, as it does not require extraction of FSII from the coating, and therefore can be performed numerous times on the same panel to evaluate a relative desorption rate of FSII as a function of time. This was performed by taking successive readings of the BMS10-39 coating after exposure to FSII, while noting the decrease in signal strength of the characteristic FSII peaks. Quantitative calibrations proved difficult due to the non-linearity of the peak heights as a function of concentration, and their variability as a function of time. Due to these factors, the data was analyzed on a relative, rather than a quantitative, basis.

Fuel Tank Topcoat Peeling (FTTP) Simulation Study

This study was designed to attempt to re-create the actual scenario for FTTP as well as quantify the effects of FSII concentrations in the fuel and ullage and temperature of fuel and condensing surfaces on resulting pencil hardness of an exposed BMS 10-39 panel. The experiment was used to test the hypothesis of DiEGME concentrating in the ullage and condensing on the topcoat surface causing degradation. This methodology could potentially determine the feasibility of using TriEGME to replace DiEGME due to its much lower vapor pressure and its decreased potential for creating a FSII rich ullage. The overall setup included a 28.3L (1ft³) aluminum box (same box used for the condensation study discussed in the Introduction) (Zabarnick et al., 2007) which contained the fuel along with a heat exchanger which was used to secure a BMS 10-39 panel. The box containing the fuel was placed inside an environmental chamber, allowing control of the fuel and box surface temperatures. The heat exchanger, placed above the fuel level, allowed for independent temperature control of the topcoat panel and the panel was secured by clamps on the edges and top of the panel. A re-circulating cooling water bath was used to control the heat exchanger temperature and the topcoat panel in contact with the cooled steel plate on the exchanger. This heat exchanger was maintained at a lower temperature than the environmental chamber to promote selective condensation only on the topcoat specimen. Figure 19 provides a schematic of this box.

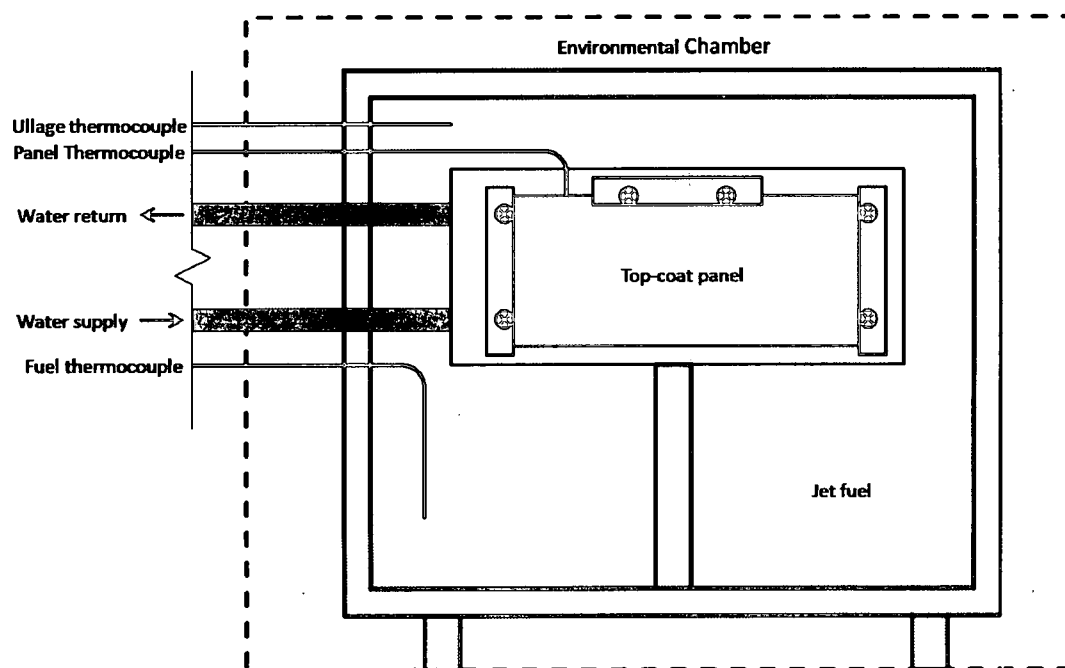


Figure 19: The FSII simulation box apparatus

The panels used with the exchanger were 3" x 6", which were larger than those used for the uptake and pencil hardness study. This was done to provide a larger surface area for contact with the condensate, and for visible confirmation of FTTP. The box was typically filled with 9L (approximately 1/3 of the total volume) of jet fuel and agitated throughout the duration of the experiment with a magnetic stir bar. This volume was used to create a similar ratio of total mass of FSII to area of topcoat as shown in the Uptake and Pencil Hardness Study, such that any absorption of FSII in the topcoat panel would not reduce the FSII concentration in the bulk fuel. Thermocouples were placed in the vapor headspace of the box, submerged into the fuel, and placed between the topcoat panel and heat exchanger surface. During the experiment, the box was closed after the fuel was added, and then the environmental chamber was heated to a given temperature. After the desired test duration (ranging from 2-5 days) and cooling to near ambient temperatures, samples of the bulk fuel and condensate were collected. The condensate samples were obtained using a chromatographic syringe to collect droplets

on the panel or the exchanger. The initial fuel sample, final fuel sample, and the condensate were analyzed by GC-MS to obtain FSII concentrations (see Quantification of FSII in Fuel Mixtures below). Data was collected while varying the initial FSII concentrations in the bulk fuel, temperatures of the box and/or heat exchanger, and the exposure durations of FSII in contact with the topcoat panel. The topcoat panel was removed from the apparatus and immediately evaluated for its hardness at five locations: the center of the panel and the four corners.

Analytical Techniques Used for Quantification

Throughout the studies used for determining the effects of DiEGME and TriEGME on topcoat compatibility, analytical techniques were developed for determining quantitative levels of FSII in water, acetone, and fuel. These techniques were used for results analysis as well as verification of solutions dosed with FSII. While there are current ASTM standards for determination of DiEGME in fuel (ASTM D5006), the technique requires a large volume of fuel (80-160 mL) which is not feasible for the studies performed here-in. In addition, the variability of the ASTM 5006 is greater than required for these studies. The analytical methods used for FSII in water, acetone, and fuel or surrogate are described below.

Quantification of FSII in Aqueous Mixtures

Some studies required verification of the FSII concentration in water before exposure to BMS 10-39. This analysis was performed by refractive index. A calibration curve was created for both DiEGME and TriEGME using a Reichert AR200 Digital Refractometer over a concentration range of 0 to 100% FSII. A Refractive Index was measured for both DiEGME and TriEGME at approximately 10 vol.% increments to generate a calibration curve, as shown in Figure 20. The reproducibility was

approximately $\pm 10\%$ of the FSII concentration. With these curves, the concentration of FSII in aqueous solutions could then be quantified.

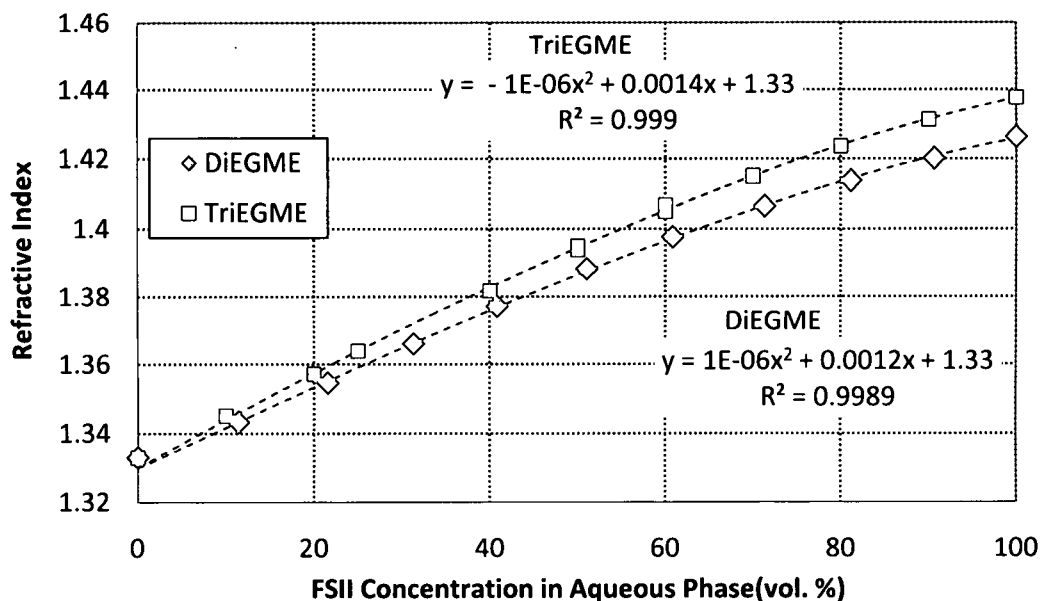


Figure 20: Refractive index calibration for DiEGME and TriEGME in aqueous solutions using a Reichart AR200 Digital Refractometer

Quantification of FSII in Acetone Mixtures

Quantifying the concentration of FSII in acetone solutions was required for the absorption study and was performed by using a Gas Chromatograph with a Flame Ionization Detector (GC-FID). A HP 5890 Series II GC-FID was used to quantify the dilute FSII component in acetone in ranges from 0-0.20 vol.%. A 1.0 vol.% FSII calibration mixture was prepared in acetone, and five samples were further diluted in acetone to 1:200, 1:100, 1:40, 1:20, and 1:4 for calibration. These dilutions encompassed the range of concentrations obtained from the uptake studies. After analysis, the area under the FSII chromatographic peak was recorded from the five calibrated samples to generate a linear calibration curve. This procedure was repeated

at least once a month to account for any changes in the calibration of the GC-FID response. Figure 21 shows representative calibration curves for DiEGME and TriEGME. Test samples from the uptake study could then be similarly analyzed and the peak area recorded to determine the FSII concentration within a reproducibility of $\pm 10\%$.

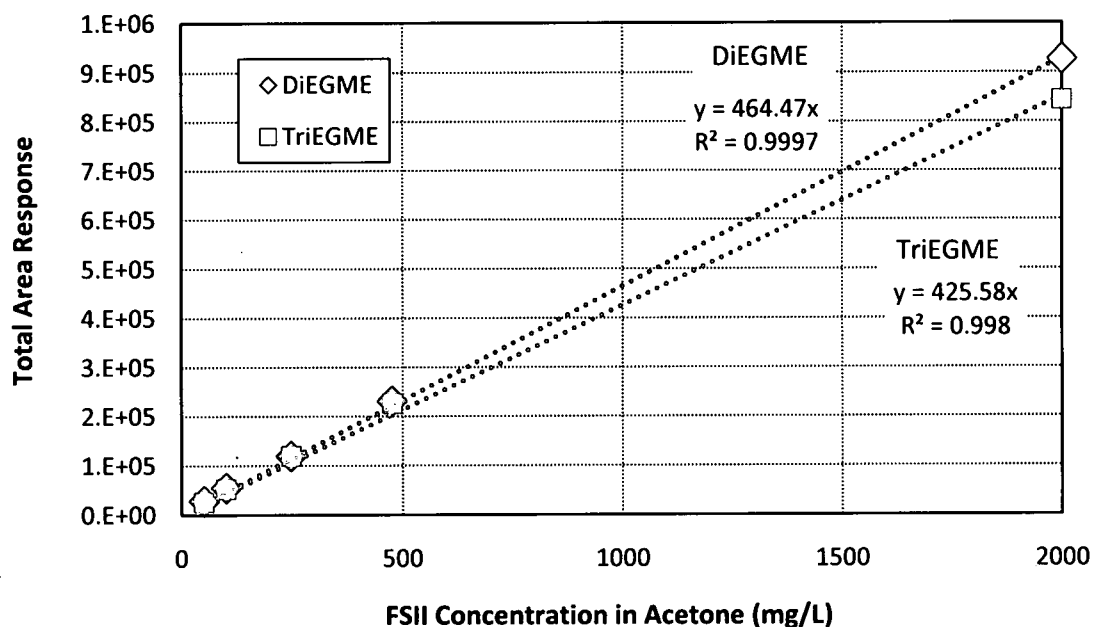


Figure 21: Calibration curves for DiEGME and TriEGME concentration in acetone mixtures

Quantification of FSII in Fuel Mixtures

For analysis where FSII is in a fuel or a fuel condensate, a more complex procedure was needed using a Gas Chromatograph with a Mass Spectrometer (GC-MS) detector. The FSII component in fuel cannot be separated and independently quantified due to co-elution with the other fuel components. To remedy this, Selective Ion Mode (SIM) is used with the GC-MS to monitor the 45, 59, and 89 ions. These ion peaks are selective for both DiEGME and TriEGME, and the FSII peak can be resolved from the resulting SIM chromatograms. The subsequent procedure is similar to the acetone quantification from this point, though the dilutions change frequently due to the larger

concentration ranges studied (0-2 vol.% FSII). The calibrations are based upon the total area response from five or more samples with known FSII concentrations. Because of the larger range of concentration, accuracy needed, and variations with the GC-MS, a single calibration curve that fit all of the data was not used. For each data set, a new curve was generated to encompass the expected concentrations. The reproducibility of this technique was approximately $\pm 5\%$ of the FSII concentration.

CHAPTER III

RESULTS AND DISCUSSION

FSII Fuel Absorption Results

Experimental studies were performed to investigate the absorption of DiEGME and TriEGME into BMS 10-39 topcoat as a function of concentration and time. The exposure studies were all performed at ambient temperatures and pressures as these conditions were representative of actual conditions and could be re-created easily. Unless specified otherwise, the panels were submerged in 20 mL FSII solutions for five days. This time was determined to be more than sufficient to achieve equilibrium, as shown by Figure 14 in the Experimental Section. The uptake data collected in Figure 22 was obtained from new panels in Jet A-1, with each FSII concentration being performed with 2-3 panels. The panels were randomly selected for each experiment, and repeatedly reused for further studies. All uptake measurements for a given concentration were performed at the same time. The topcoat volume was estimated based upon the density of new BMS 10-39 topcoat, and the average thickness of the coating. The "Concentration level of failed topcoat flakes" line is an uptake measurement obtained from failed flakes from the field. These failed topcoat flakes which were obtained from B-52 aircraft were analyzed by the same acetone extraction methodology as used to analyze the test samples during the absorption studies. Three separate flakes were analyzed in this fashion and the level of DiEGME was averaged with a reproducibility of $\pm 20\%$ of this concentration.

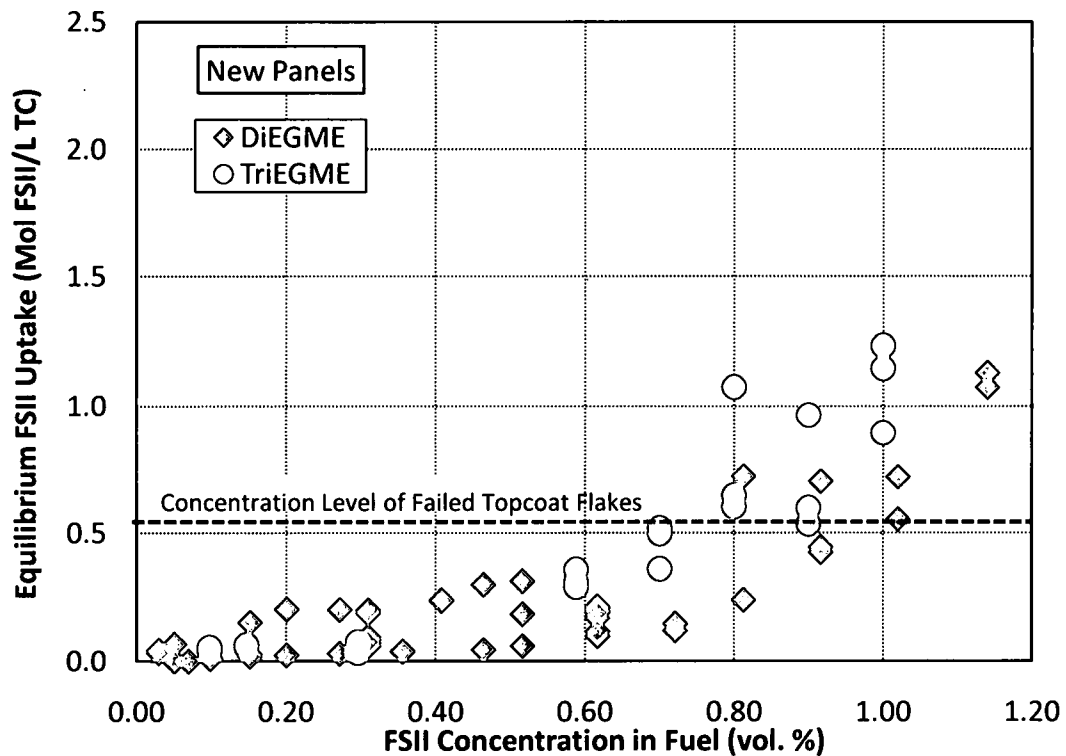


Figure 22: The equilibrium uptake of new panels exposed to DiEGME and TriEGME in Jet A-1

There are a number of key points that can be extracted from this set of data. Increasing the initial concentration of FSII in the fuel increases the quantity of FSII absorbed into the topcoat layer. The increase occurs significantly at concentrations greater than 0.50-0.80 vol.% FSII. Both DiEGME and TriEGME performed similarly and followed the same trend. The uptake from the failed topcoat flakes was determined to be approximately 0.66 mol FSII/L topcoat. The FSII uptake increases above the level of failed topcoat flakes at approximately 0.80 vol.% FSII in the fuel. This suggests that the concentration in the fuel required for failure to occur is at least 0.80% FSII in cases of direct contact, though additional analysis and correlation with topcoat integrity (e.g., pencil hardness) is needed for verification. It is highly likely that the concentration of FSII in these flakes has decreased over time due to handling and evaporation from the coating. The reproducibility of the absorption data can be fairly poor at some

concentrations, with the data varying up to $\pm 100\%$ of an averaged concentration. There are a number of factors that contribute to this including variations in the GC analysis, slightly unequal topcoat thickness, and possibly slight degradation of the topcoat after repeated use of some panels. Variations in the topcoat due to degradation or unequal thickness most likely contributed to the low reproducibility, as any change in the volume of the topcoat will have a large impact on the uptake value.

The absorption of FSII into BMS 10-39 was also analyzed using the older panels to provide an understanding of possible changes that can occur in the topcoat after 40 years of contact with fuel. This analysis provides a scenario that may better replicate the current stresses the topcoat is under in B-52 aircraft. The absorption data for old panels in fuel is shown in Figure 23 under ambient temperatures and an exposure time of five days.

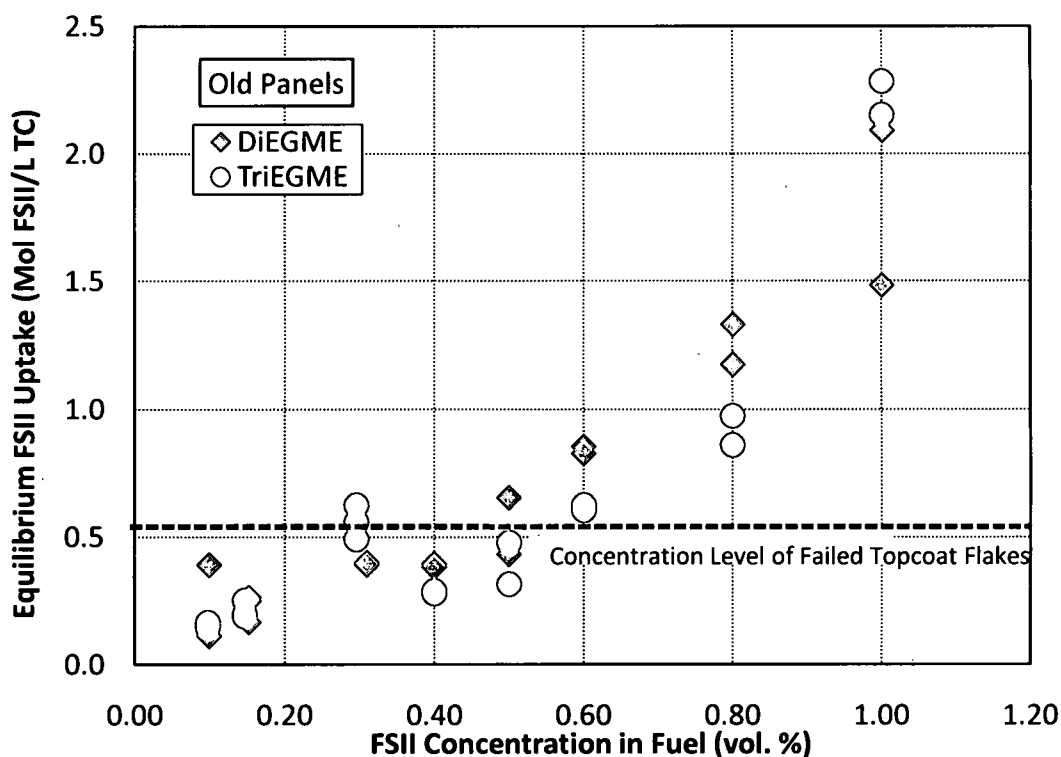


Figure 23: The uptake of DiEGME and TriEGME in Jet A-1 obtained by old panels that were in service for 40+ years

Using older panels resulted in a significant increase in the topcoat uptake relative to the newer panels. This result can be explained by the old topcoat having a reduced resistance to absorption due to weakening of the polymer matrix which allows more molecules to enter within the coating. As shown in Figure 22 with the new panels, a concentration of 0.80 vol.% FSII in the fuel was necessary to reach an uptake value higher than the failed topcoat flakes. Older panels show a decrease in the minimum concentration of FSII to reach this same uptake value, as low as 0.50 vol.% FSII. The concentration level of failed topcoat flakes is well below the uptake obtained by higher concentration of FSII in the fuel. This is most likely due to DiEGME desorbing from the topcoat flakes to a lower long-term concentration.

DiEGME and TriEGME have shown similar extents of absorption in both the old and new topcoat panels on a molar basis. On a mass basis, TriEGME has a higher equilibrium uptake than DiEGME. This can be explained by the molecular weight of TriEGME (164 g/mol) being one-third higher than DiEGME (120 g/mol), and the absorption being a function of the number of molecules BMS 10-39 can absorb, not mass. While the new and old panels show a similar trend for this absorption study, the old panels appear to represent a worst-case scenario due to the increased equilibrium uptake.

Overall, the FSII absorption in Jet A-1 results show a very strong relationship between the concentration of FSII in the fuel and the absorbed concentration into BMS 10-39. This relationship was present in both new and old panels, with the difference being a much larger equilibrium uptake occurring with the older panels. This data is similar to the JP-8 data obtained by Aliband et al. (2006), from Figure 7 (Related FTTP Research), which used old topcoat flakes. Their data covers a much larger range, possibly beyond the solubility limit of DiEGME in fuel, but overall shows a similar trend. Initially the JP-8 data shows a 6% ESU uptake from 0 to 0.75 vol.% DiEGME in the fuel,

and then increases rapidly. The data obtained via acetone extraction to solely quantify the absorbed FSII shown in Figure 23, does not show any uptake in the topcoat with neat Jet A-1 fuel. The higher uptake observed by Aliband et al. (2006) is possibly a function of other fuel components partitioning into the topcoat. After a sufficient concentration of DiEGME is achieved in the fuel, the absorption appears to become predominately due to DiEGME, and the two data sets match more closely.

FSII Aqueous Absorption Results

Further experimentation was performed with DiEGME and TriEGME to determine the absorption of FSII from aqueous solutions to better understand the occurrence of FTTP occurring at the water bottoms of fuel tanks. This data will serve to investigate the relationship between FSII concentration in the aqueous mixtures and the molar uptake within the topcoat. This analysis was performed at ambient temperatures with the panels exposed to the aqueous solutions for five days. Figure 24 shows the combined graphs for new and old panels with each data point representing the average of 2-3 uptake measurements.

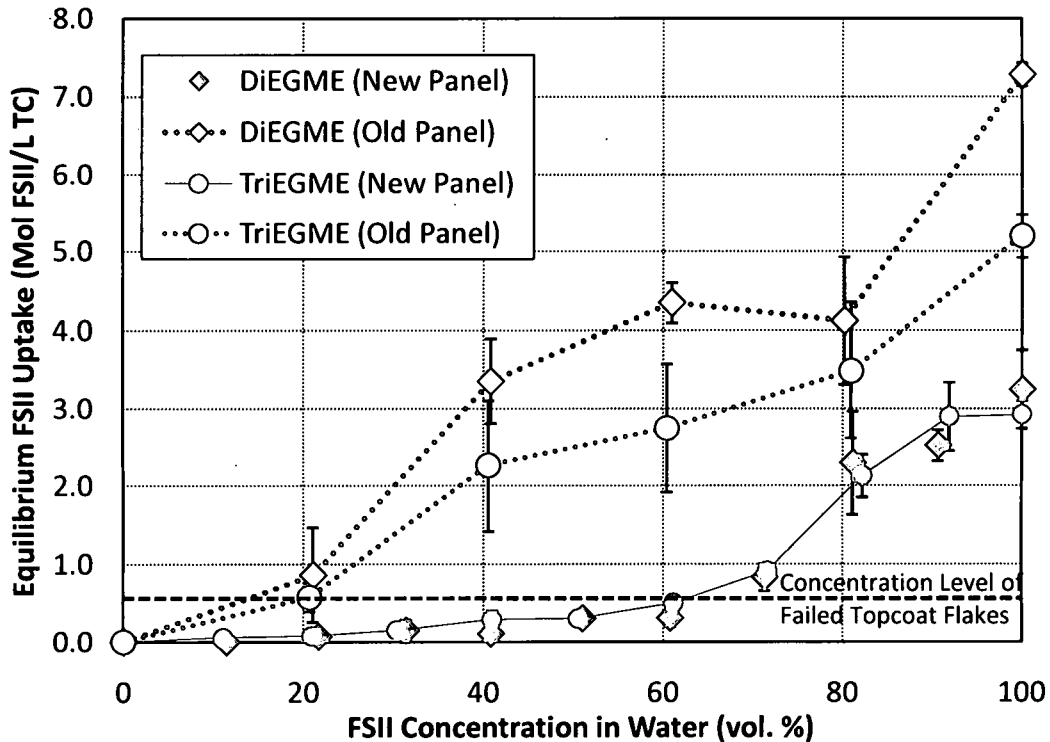


Figure 24: The uptake of DiEGME and TriEGME with new and old panels in aqueous solutions

A similar trend is observed with aqueous solutions compared to fuel. The new panels show very little uptake until a critical concentration of approximately 70 vol.% FSII is achieved, while the uptake for older panels continuously increases with increasing FSII concentration in a somewhat linear trend. At concentrations greater than approximately 80 vol.% FSII, the new panel uptake appears to plateau, or at least not increase as rapidly. This trend is almost identical to the aqueous ESU data obtained by Aliband et al. (2006). Their data shows a distinct "S" shaped curve with the ESU measurements reaching a plateau after 75 vol.% DiEGME in the water.

The newer panel absorption in Figure 24 elevates above the failed topcoat flakes concentration at 70 vol.% FSII, while the old panels achieve this at a lower concentration of approximately 20 vol.% FSII. Again, the older panels absorb more FSII than the newer panels as shown by both the aqueous and fuel absorption studies. Overall, the

aqueous solutions have shown a much higher maximum uptake than the initial concentration range investigated for FSII in fuel solutions. The maximum concentration for aqueous solutions was approximately 7.2 mol FSII/L TC at 100 vol.% FSII, while the maximum concentration for fuel exposures was approximately 2.2 mol FSII/L TC at 1.0 vol.% FSII. This increase in uptake is simply explained by the much higher concentration of FSII in the aqueous solutions, which alters the equilibrium to an increased FSII concentration in the topcoat. While the topcoat was still physically intact after exposure to 100% solutions of DiEGME and TriEGME, it was easily damaged with contact.

In order to evaluate the relative desorption rate of FSII from the topcoat polymer matrix, as well as provide a comparison for DiEGME and TriEGME, the original uptake experiment was slightly altered. Instead of immediately placing the topcoat panels in the acetone extraction after exposure, they were allowed to dry in a fume hood at ambient temperatures for a pre-determined period of time. The uptake for an aqueous concentration range of DiEGME was collected as a function of time and is shown in Figure 25.

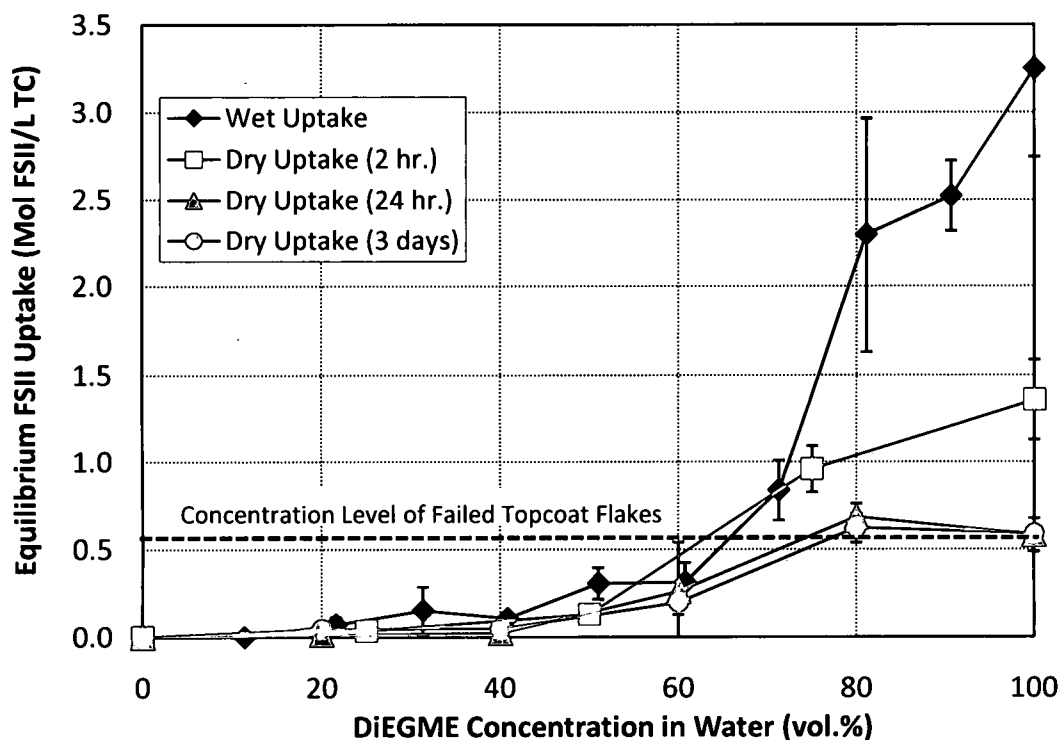


Figure 25: The uptake of DiEGME in aqueous solutions after a given period of drying time with new panels

The figure shows that the concentration of DiEGME in the topcoat decreases as more time is allowed for desorption. Except for DiEGME concentrations greater than 70 vol.% in water, the equilibrium uptake is very similar for the four tested time periods. Initially, there is a very large decrease in the DiEGME absorbed in the topcoat in only a couple of hours at concentrations greater than 70 vol.% in the water, and then the desorption rate slows down significantly. The DiEGME concentration in the coating reaches its final equilibrium level in less than 24 hours. It is interesting to note that DiEGME does not completely desorb from the topcoat, and the resulting final concentration of DiEGME in the topcoat is identical to the uptake level from the failed topcoat flakes at approximately 0.66 mol FSII/L topcoat for concentrations greater than 80 vol.% in the water. In order for the dried flakes to have such a high concentration, they must have been exposed to an even greater concentration of DiEGME initially.

Once the topcoat is exposed to a sufficient concentration of FSII to cause a failure, it is possible the FSII in the coating will always desorb to this uptake level.

The desorption experiment was repeated with TriEGME as the FSII component to further analyze TriEGME as an adequate anti-icing additive. Under identical conditions with the same sample size and exposure time, the results for this experiment are shown in Figure 26.

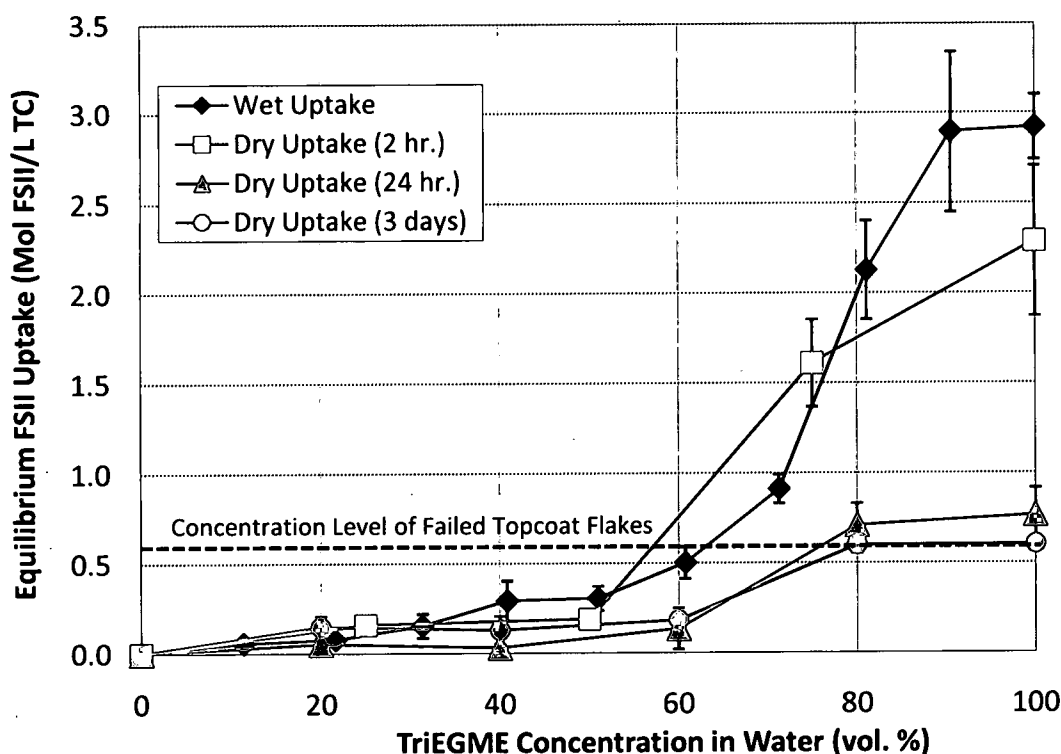


Figure 26: The uptake of TriEGME in aqueous solutions after a given period of drying time with new panels

The desorption trends were observed to be very similar for both DiEGME and TriEGME. The equilibrium uptake of TriEGME as a function of time is equivalent up to a concentration of 50 vol.% TriEGME. Above this concentration, it is evident desorption is occurring. As more time is allowed for TriEGME to desorb before the acetone extraction, the equilibrium uptake of the topcoat decreases. Both DiEGME and TriEGME initially desorb rapidly, though there is a significant difference between the two

additives after two hours at the 100 vol.% TriEGME exposure. While the DiEGME concentration is reduced to 42% of the original concentration after two hours, TriEGME is only reduced to 78%. This difference can be accounted for by the lower vapor pressure of TriEGME, which will not vaporize as readily from the topcoat. The slower rate of TriEGME desorption may also be a result of the larger molecular size slowing diffusion of the molecules through the polymer matrix. Based upon Figure 25 and 26, both DiEGME and TriEGME can desorb to a similar concentration level if given an appropriate amount of time.

Overall, TriEGME and DiEGME both absorb similarly into the topcoat with respect to the final equilibrium uptake, though the desorption rate is different. This initial difference in desorption rates at high concentrations of FSII could potentially lead to some complications, as it would be possible for potential FTTP concentration of TriEGME in the topcoat to be maintained for longer periods of time. However, it is hypothesized that these high concentrations of TriEGME which yield high uptake levels and severe swelling in the topcoat will not be achieved due to a lower vapor pressure reducing the concentration in the condensate. This study was not able to fully evaluate the FTTP process; however it provided insight into what concentration of FSII in Jet A-1 or water will promote swelling and high absorption levels.

IR Spectroscopy Results

In an effort to further investigate the desorption rates of DiEGME and TriEGME from BMS 10-39 in a non-destructive manner after exposure, Attenuated Total Reflectance Infrared Spectroscopy (ATR-IR) experiments were performed. As discussed in the Experimental section, spectra were taken of the newer panels after being exposed to pure solutions of DiEGME or TriEGME. It should be noted the infrared radiation will only penetrate a couple of microns dependent upon the organic coating.

Because of this, the ATR-IR is considered to evaluate the surface concentration of FSII in BMS 10-39 and is not representative of the entire coating. Figure 27 shows the ATR-IR results for a topcoat panel exposed to DiEGME with the transmittance as a function of time.

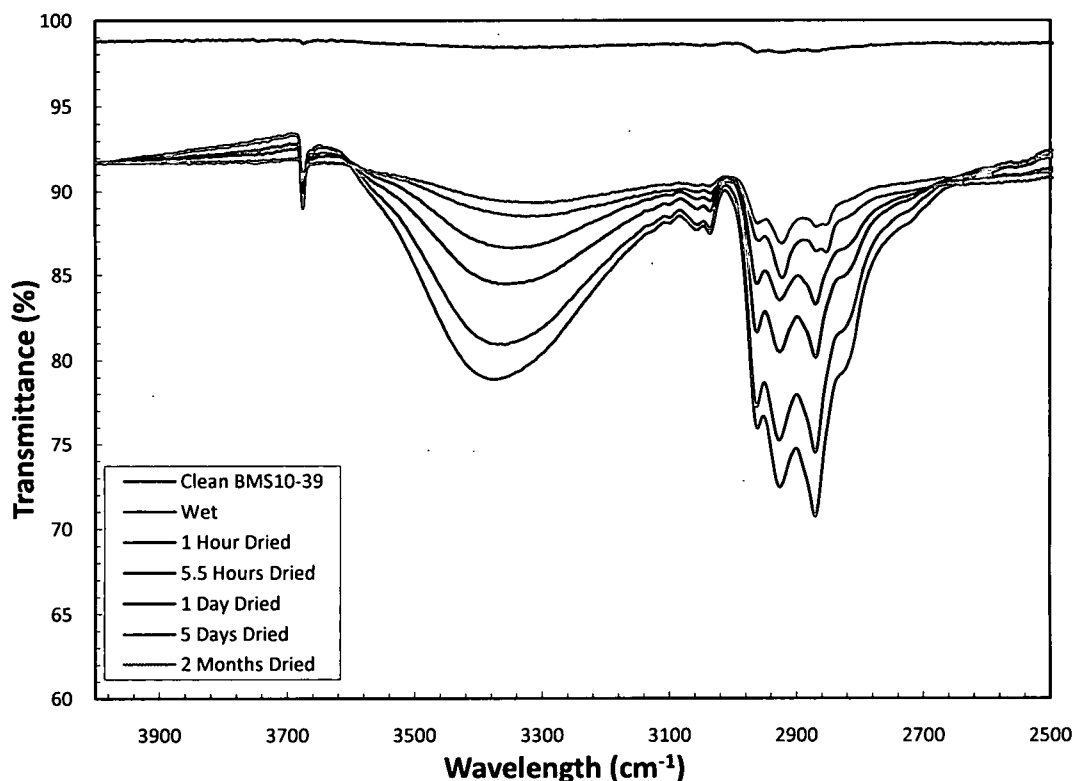


Figure 27: IR spectrum of a new BMS 10-39 panel exposed to pure DiEGME as a function of time

This work focuses on the wavelengths from 4000 to 2500 cm^{-1} in order to get a closer look at how the signal decreases with time for two specific peaks. The broad peak at approximately 3400 cm^{-1} indicates the presence of O-H bonding, while the sharp peaks from 3000 to 2800 cm^{-1} represent C-H₂ and C-H₃ bonds. The fingerprint region (1700 to 600 cm^{-1}) did not provide much insight into the evaporation of FSII out of the topcoat as peak heights became convoluted and difficult to interpret. From Figure 27, it is evident there is a decrease in the peak heights over time, which is related to the

concentration of DiEGME in the panel. The rate of evaporation is rapid during the first couple of hours to days, and then slows beyond that. There is not as much change after five days to a month. This supports the uptake data shown earlier. The peak heights also do not return to the original BMS 10-39 background, which shows that DiEGME never fully evaporates out of the coating. This qualitative data supports the uptake data along with the concentration level of DiEGME in the failed topcoat flakes. Initially, quantitation was attempted based upon the peak heights relative to the baseline to correlate to an uptake measurement. However, it was difficult to calibrate and the peak heights were dependent on time as well as the FSII concentration. Due to these difficulties, the data was evaluated relative to the TriEGME desorption in addition to the quantitative data obtained from the desorption uptake data. This work has shown that DiEGME will evaporate out of BMS 10-39; however, not all of the DiEGME will be removed from the coating.

The ATR-IR experiment was repeated with newer panels exposed to a 100% solution of TriEGME to draw a comparison between the two FSII additives, as shown in Figure 28.

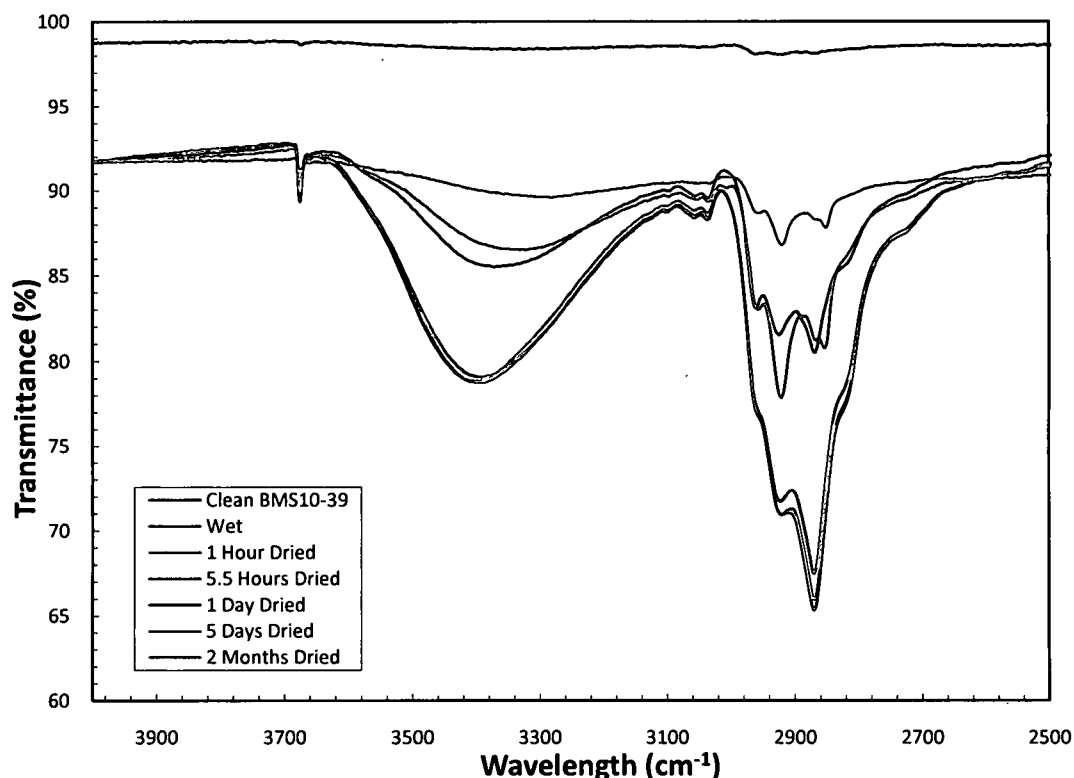


Figure 28: IR spectrum of a new BMS 10-39 panel exposed to pure TriEGME as a function of time

TriEGME displays slightly different results for the ATR-IR data relating to the evaporation rate from the topcoat. There is no reduction in the signal strength of the TriEGME peaks after the first 5.5 hours of evaporation. This is followed by a decrease in concentration of FSII in the topcoat after 1 day of drying. The subsequent spectra taken after 1 day continue to slowly decrease in a similar fashion to DiEGME. After two months of drying, both DiEGME and TriEGME reach the same signal strength, which for the 3400 cm^{-1} wavelength peak is at approximately 90% transmittance. As shown in the uptake data, TriEGME is able to reach the same concentration in the topcoat, although it is a slower process. Considering TriEGME has a vapor pressure an order of magnitude lower than DiEGME, as well as a larger molecular size, this would cause it to desorb and vaporize more slowly out of the topcoat. Using ATR-IR, the time taken for a final FSII concentration to be reached was shown to be between five days and two months, while

the uptake data shows approximately one day. This difference is partially due to the location at which the panels are dried. While the uptake panels dried in a well circulated fume hood, allowing for a quick vaporization of any FSII desorbed to the surface, the ATR-IR panels dried on a counter top in a typical room. ATR-IR also measures the surface concentration of FSII in the topcoat, while the uptake studies evaluate the concentration in the entire topcoat.

This data supports the trends shown in the desorption experiments. The evaporation of TriEGME is initially slower than that of DiEGME, however the uptake concentrations and transmittance become equivalent for both studies after a significant period of time has elapsed. This difference in desorption rates could cause some problems, as potentially high concentrations of TriEGME in the topcoat will be maintained for a longer period of time, which could increase the chance of swelling and the occurrence of FFTP.

ATR-IR was also used to verify that the acetone extraction step from the absorption study removed any detectable levels of the FSII. A spectrum of a clean BMS 10-39 panel was compared with one that had been recently exposed to acetone to remove the absorbed FSII. These two spectra were almost identical, and showed that the acetone was at least able to extract the absorbed FSII in the surface of the coating.

Pencil Hardness Study Results

Further studies were performed to evaluate the topcoat integrity after the absorption of FSII has occurred. These provide valuable insight into what concentration ranges of FSII in fuel or water provide sufficient absorption to cause FFTP. The exposure duration for the Pencil Hardness study was two days, which was shorter than some uptake studies. This was done in order to be able to complete measurements in a reasonable test time, while still maintaining the minimum exposure duration for

equilibrium. Each pencil hardness data point represents a single panel that was tested at the given FSII concentration. This first study used the surrogate condensate discussed in the experimental section which attempts to simulate the lighter components observed in headspace above the fuel. As it is hypothesized that the condensed vapors are the bulk component in contact with the fuel tank walls where FTTP has occurred, this surrogate is used to more accurately investigate this phenomenon. Figure 29 shows an overlay of the equilibrium uptake and pencil hardness of new panels in a surrogate as a function of the FSII concentration.

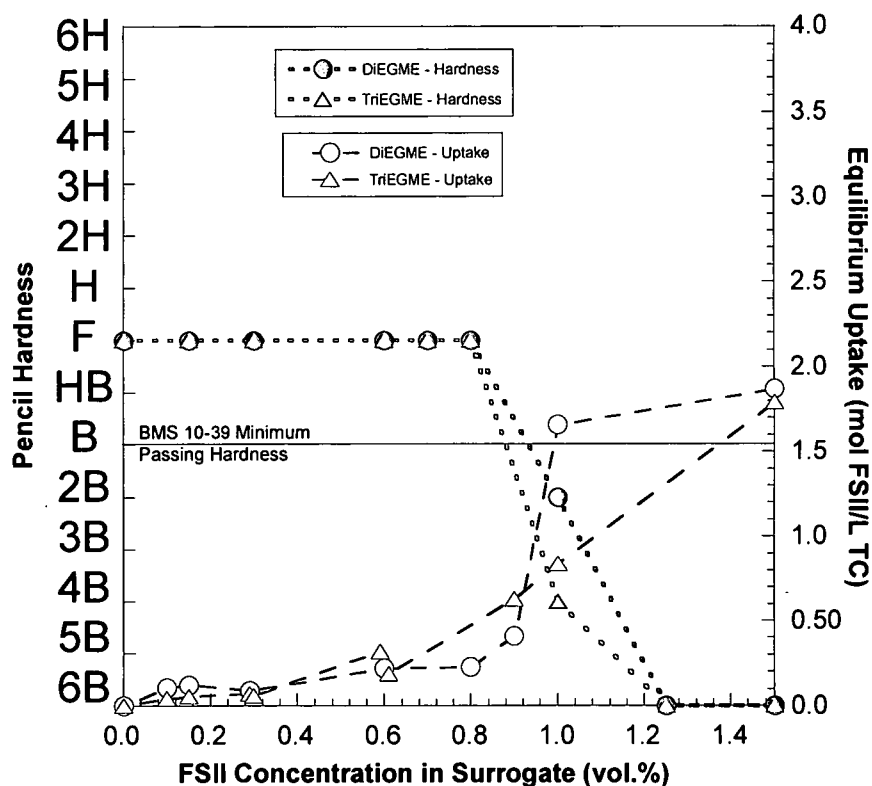


Figure 29: New panel uptake and wet pencil hardness in a fuel condensate surrogate

Figure 29 shows a very strong relationship between the pencil hardness of BMS 10-39 and the equilibrium uptake. The pencil hardness of the panel is unaffected by increasing FSII concentration, until the uptake begins to increase dramatically at

concentrations greater than 0.80 vol. %. As the uptake increases, a very sharp decrease is observed in the pencil hardness. The BMS 10-39 panels at concentrations greater than 1.0 vol.% FSII are easily damaged beyond this point. Both DiEGME and TriEGME behave very similarly in this pencil hardness experiment. The largest difference occurs during the transitional range (0.80 – 1.20 vol.%), where the TriEGME pencil hardness is three pencil leads lower than DiEGME. Considering a reproducibility of ± 1 pencil lead based upon the ASTM D3363 with hardness testing, the results are very similar, but not equivalent. From Figure 29, the equilibrium uptake level corresponding to the degradation of BMS 10-39 occurs at uptakes greater than approximately 1 mol FSII/L topcoat. The topcoat integrity continues to decrease and loses adhesion as the concentration in the topcoat increases further.

Using a surrogate instead of fuel raised questions concerning the possibility of different interactions between BMS 10-39 and Jet A-1 or the fuel condensate surrogate. While the uptake data from Figure 29 is very similar to the fuel uptake shown in Figure 22, the pencil hardness differences have not been evaluated. In order to investigate this, pencil hardness data for Jet A-1 and surrogate testing was combined with the uptake data. Figure 30 shows the uptake of Jet A-1 and the fuel condensate overlaid with the wet pencil hardness measurements.

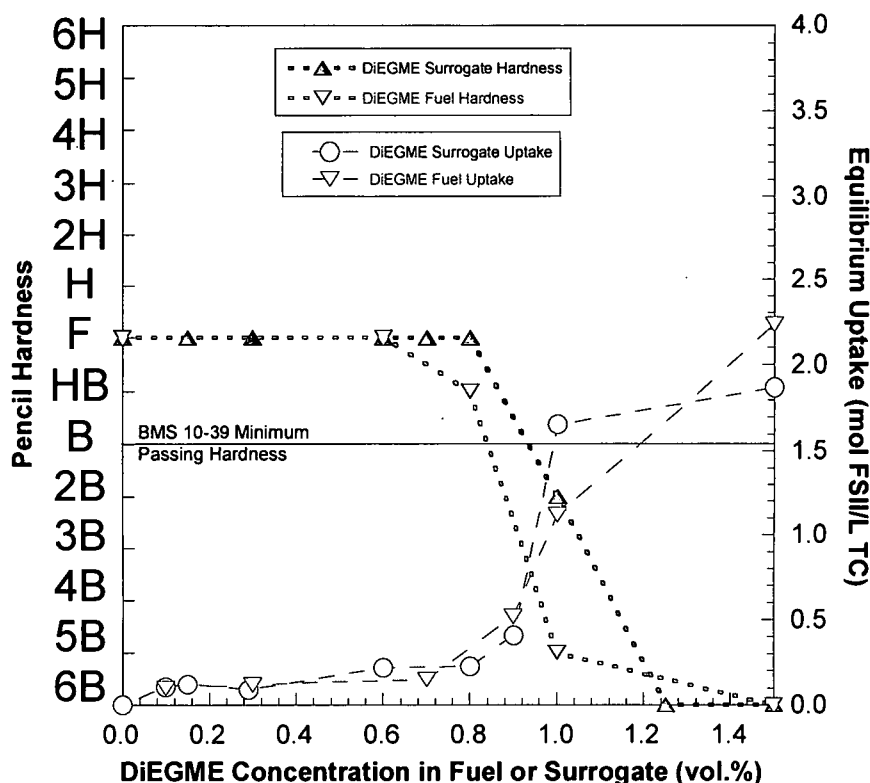


Figure 30: Comparison of the uptake and pencil hardness of new panels after exposure to Jet A-1 and surrogate solutions with varying DiEGME concentrations

It is clear there is little difference between the absorption and pencil hardness of FSII in Jet A-1 and the surrogate. Both the fuel and the surrogate have uptake that dramatically increases at concentrations greater than approximately 0.8 vol.% FSII, with a concurrent decrease in the pencil hardness. The hardness of the topcoat exposed to Jet A-1 solutions does begin to degrade at lower concentrations of FSII. This difference is not very large however, and there is also some uncertainty with the pencil hardness data. As discussed previously, the pencil hardness procedure is subject to numerous uncertainties with a reproducibility of ± 1 pencil lead. Since both fuel and a surrogate produce similar results, the surrogate was used for further pencil hardness studies in an effort to create a more realistic scenario for the conditions of FTTP.

Pencil hardness measurements were taken with old panels as well to determine what effect the increased uptake will have on the hardness of the topcoat. If the older panels represent a worst-case scenario for the current BMS 10-39 coating in B-52 aircraft, then studying the pencil hardness of these panels after exposure to FSII is critical for investigating the requisite conditions for FFTP. Pencil hardness measurements were taken using old BMS 10-39 panels under identical conditions as the previous experiments. The results are shown in Figure 31, overlaid with the uptake from old panels in the condensate surrogate.

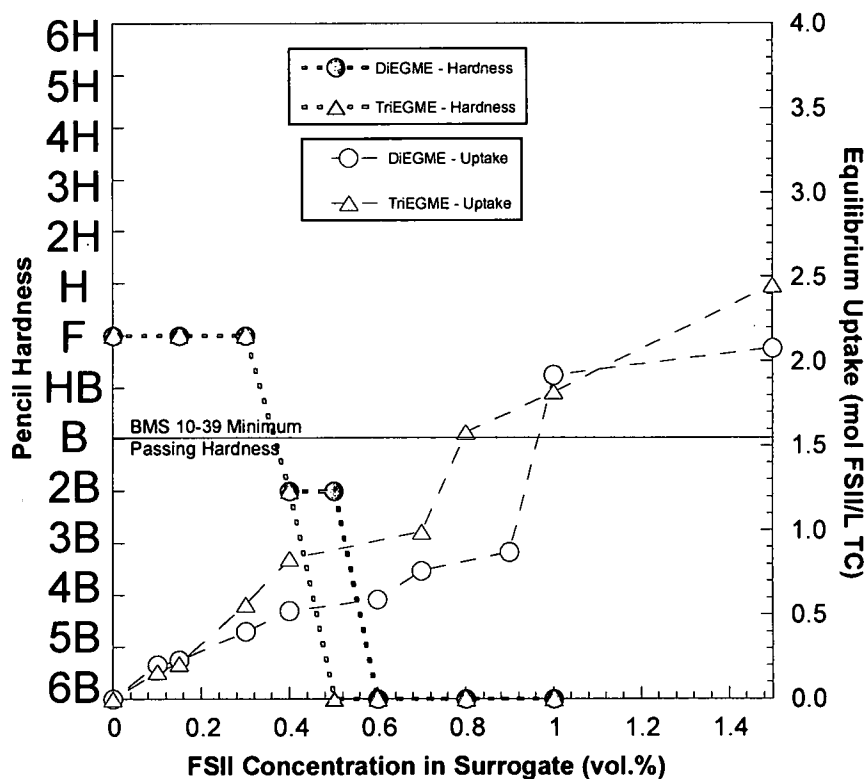


Figure 31: The uptake and pencil hardness of DiEGME and TriEGME in a surrogate with old panels

The pencil hardness begins to decline rapidly at approximately 0.30 vol.% FSII, which corresponds with an increase in the uptake. This FSII volume percent is only twice the maximum procurement concentration for JP-8. The pencil hardness falls

below the minimum passing rating of 'B' at a FSII concentration of approximately 0.40 vol.% FSII in the surrogate. This is a significant decrease from the concentration necessary to fail newer panels (approximately 1.0 vol.% FSII). Overall, the older panels show highly decreased properties in regards to maintaining the coating hardness and resistance to fluid transport, evident by the increased absorption of FSII. While newer panels continue to show similar trends between DiEGME and TriEGME, older panels should be used for analyzing extremely conservative scenarios. This is due to the reduced properties of the topcoat after constant exposure to fuel and possibly environmental conditions. These older panels begin to have increased void spaces and weakened polymer bonds from constant fuel or FSII molecules stretching the bonds within the matrix.

Pencil hardness testing was adapted to investigate the effect of FSII desorption from the topcoat evident from the uptake and ATR-IR studies. Instead of evaluating the hardness immediately after removal from the solution and "blot-drying", they were tested after drying two hours in a fume hood. This study was performed using the condensate surrogate and new panels at ambient conditions. The data is shown in Figure 32. It should be noted the additional uptake data included in Figure 32 was not obtained from dried panels in a similar fashion to the pencil hardness panels.

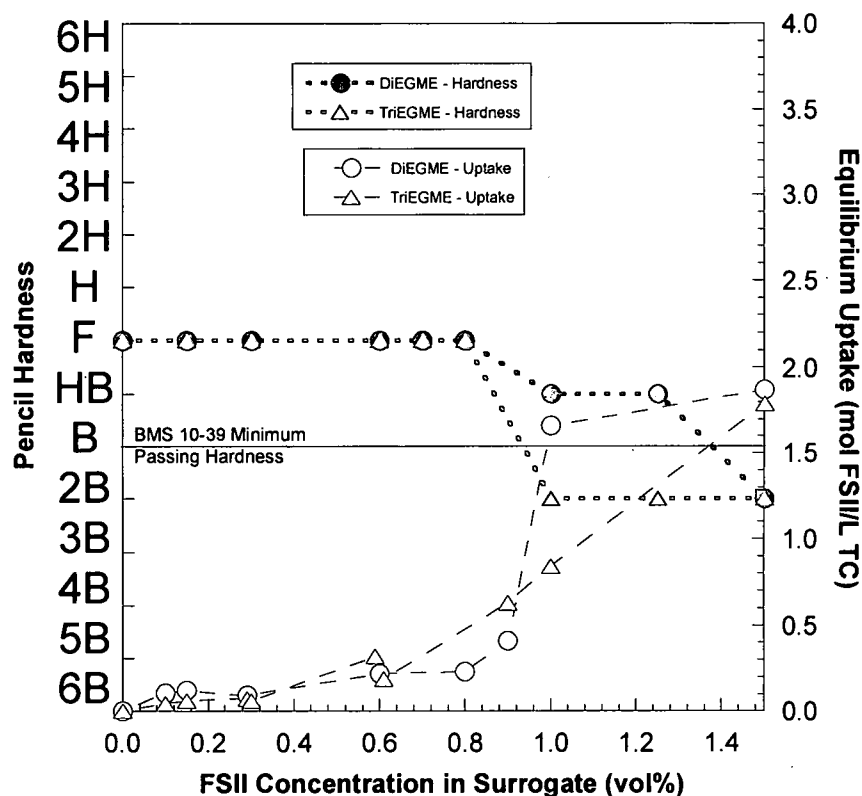


Figure 32: Pencil hardness for new panels in surrogate after two hours and “wet” uptake data

The pencil hardness of DiEGME and TriEGME still decreases as the concentration of FSII in the surrogate increases, however the hardness does not decrease to nearly the same extent as the panels evaluated immediately after contact with FSII. Panels exposed to DiEGME remain above the minimum passing hardness for BMS 10-39, except for 1.5 vol.% DiEGME in the surrogate; panels exposed to TriEGME fall below the minimum at a concentration of 1.0 vol.%. When the panels were evaluated while “wet,” exposure to both DiEGME and TriEGME decreased the hardness at the same concentration of 1.0 vol.% FSII. As discussed above, this difference could be due to the lower vapor pressure of TriEGME, which initially causes it to desorb and evaporate more slowly from the coating as shown by the uptake and ATR-IR studies. Considering the uptake and ATR-IR data, it would be expected for the pencil hardness to

reach the same level in both DiEGME and TriEGME if more time is given for desorption to occur. This data shows that BMS 10-39 exposed to high concentrations of TriEGME will have a reduced hardness for a longer period of time compared to DiEGME. This could potentially increase the timeframe for FTTP to occur.

In order to further study FTTP, the pencil hardness was evaluated for new BMS 10-39 panels after exposure to aqueous solutions. Similar to the fuel and surrogate pencil hardness testing, this provides insight into the requisite concentration levels in water bottoms necessary for degradation to occur. Figure 33 shows the "wet" pencil hardness testing and uptake as a function of FSII concentration for new panels in aqueous solutions.

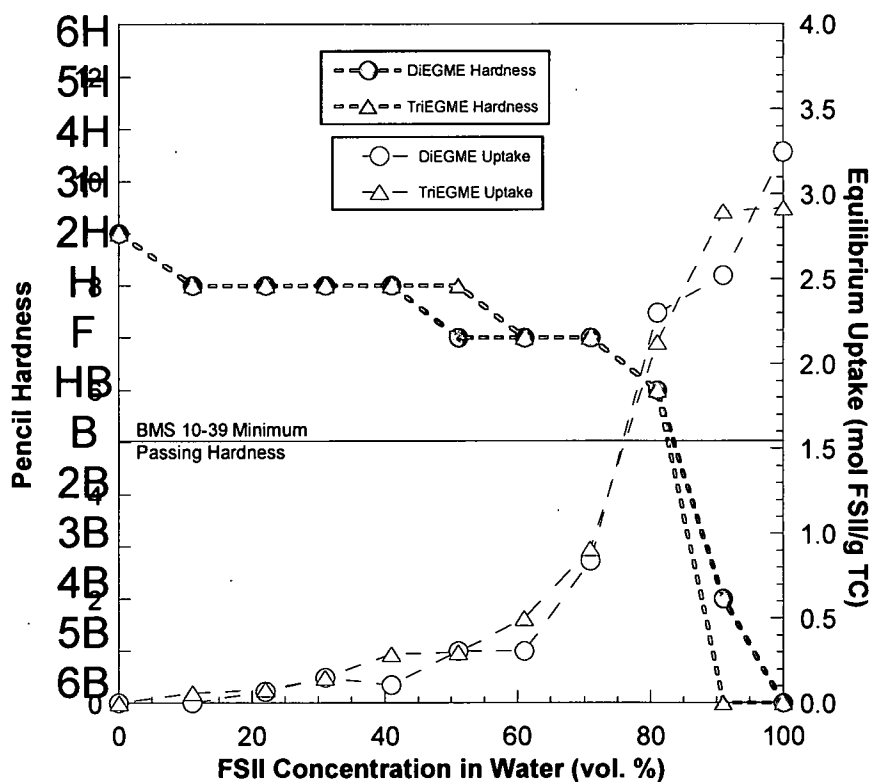


Figure 33: Pencil hardness and equilibrium FSII uptake of new panels in aqueous solutions with varying concentrations of FSII

The uptake dramatically increases at approximately 70 vol.% FSII, while the pencil hardness also begins to decrease rapidly. New topcoat in a surrogate or fuel have been shown to degrade at approximately 2.0 mol FSII/L topcoat and the aqueous solutions also show a very similar uptake concentration for failure. This degradation seems to require concentrations greater than 70 vol.% DiEGME or TriEGME in water in contact with the topcoat. This is much higher than expected (30-50 vol.%) in tank bottoms at ambient conditions with correct FSII levels in fuel. The initial hardness of these panels exposed to aqueous solutions was slightly higher than those exposed to fuel surrogate solutions. While there was some variation with the initial hardness from both the new and old panels used, the surrogate alone seemed to have a very slight softening effect of 1 pencil lead on the topcoat. This could potentially be due to some slight swelling due to absorption of unknown fuel species into the BMS 10-39 coating.

Overall, pencil hardness testing has been able to provide a comparison between DiEGME and TriEGME, which has shown statistically identical behavior for most of the study. It has also provided a greater understanding into what concentrations are necessary to achieve, or at least initiate, FFTP. Based upon the measured topcoat failure of new panels in a fuel or surrogate, concentrations of FSII greater than 1.0 vol.% are required to severely weaken the topcoat. Older panels only require concentrations of FSII greater than approximately 0.40 vol.% FSII in the fuel or surrogate to degrade the topcoat below the minimum hardness of 'B'. As discussed above, this difference in concentration is a result of the reduced capabilities of the older panels to resist FSII absorption. The new panels and old panels used seem to represent the best and worst case scenarios which would be expected in a B-52. Aqueous solutions require concentrations greater than 80 vol.% for newer panels to cause a failure. The AFRL CTIO office has performed hardness testing in their evaluation of DiEGME and TriEGME, though all of their aqueous exposures at 80 vol.% resulted in the topcoat

completely degraded and eroded from the aluminum substrate (Hufnagle, 2008). Their conditions for exposure were very different from what was used in the pencil hardness study. The exposure times included 7, 14, and 60 days while at a temperature of 60°C. While the aqueous solutions were not comparable, the CTIO results for their pencil hardness measurements after exposure to surrogate solutions showed very similar trends with the pencil hardness study. The DiEGME data is within one to two pencil leads from Figure 32, though the CTIO results are consistently higher for the three data points obtained from Figure 12 (Recent FTTP Research). For example, at a concentration of 1.50 vol.% DiEGME in the surrogate, Hufnagle (2008) reports a hardness of 'HB' while Figure 32 reports a hardness of '2B'. The slightly higher pencil hardness rating could be due to operator variability or possibly a result of a more thorough wash and rinse of the topcoat panel after exposure at the CTIO office. Their wash includes thorough rinses with bleach solutions, tap water, and DI water. The TriEGME data reported by Hufnagle (2008) is also higher than what is reported in Figure 32, though the different methodologies or user variabilities are applicable again. Overall, these two surrogate studies showed a very similar trend for the hardness of BMS 10-39 panels after two hours of drying.

From the pencil hardness study, there were no clear differences between the hardness of BMS 10-39 panels after exposure to DiEGME and TriEGME, except in the case of allowing the panels to dry after exposure before performing hardness testing. The increased hardness of DiEGME in this scenario is most likely due to its higher vapor pressure, which is supported by the desorption and ATR-IR studies. Because there is less FSII remaining in the topcoat, there is less swelling and the coating retains a higher hardness. While DiEGME and TriEGME performed similarly in this study, different pencil hardness results are expected when the vaporization process of FSII in the bulk fuel is combined with the condensation process of the FSII rich solution onto the topcoat.

It would be expected for TriEGME to have a much lower concentration (in contact with the BMS 10-39 panel) compared to DiEGME, because of its reduced vapor pressure.

Fuel Tank Topcoat Peeling (FTTP) Simulation Results

A simulated B-52 fuel tank environment was used to attempt to re-create all aspects required for FTTP as well as fully evaluate TriEGME as a replacement FSII based upon its lower vapor pressure. Zabarnick et al. (2007) have performed one such experiment that directly compared the concentrations of DiEGME and TriEGME in the fuel condensate after vaporization from the bulk fuel. The results, which were shown in Figure 10 (Related Fuel Tank Topcoat Peeling Research), provided evidence that the concentration of DiEGME in the condensate increased with each distillate fraction and further vaporization, while the concentration of TriEGME in the condensate maintained a level below the initial concentration in the bulk fuel. While this previous experiment focused on collecting the fuel condensate in an environmental chamber, the FTTP simulation will promote condensation of the FSII on an old topcoat panel, which is then evaluated for its hardness. This simulation of a fuel tank was designed to re-create all primary steps for FTTP to occur in a controlled setting. It also functions to investigate the effects of specific variables on FTTP, such as the initial concentration of FSII in the bulk fuel, the temperature of the environmental chamber, and the temperature of the condensing topcoat surface. Selective condensation on the topcoat panel was achieved by using a heat exchanger with a recycling cooled water bath. The concentration range of FSII initially in the fuel used for this experiment was from 0 to approximately 0.15 vol.%, while the temperatures investigated were 50 or 60°C in the environmental chamber, and a cooling surface of 10 to 30°C. These ranges of concentrations and temperatures were used as they are believed to accurately represent the conditions of a B-52 fuel tank. Fuel and condensate samples were collected and quantified for their

DiEGME or TriEGME concentration after three to five days of condensate exposure on the topcoat. This was shown to be sufficient for equilibrium to be reached, which is discussed below. The data collected from this set of experiments at a fuel temperature of 60°C and a cooling surface temperature of 20°C along with the quantified FSII concentrations is summarized in Table 2. Figure 34 presents the pencil hardness data as a function of the initial concentration for the experimental conditions in Table 2.

Table 2: DiEGME and TriEGME experimental runs with the environmental chamber at 60°C and the condensation surface at 20°C

Initial DiEGME Conc. (vol.%)	Final DiEGME Conc. (vol.%)	Condensate DiEGME Conc. (vol.%)	Initial TriEGME Conc. (vol.%)	Final TriEGME Conc. (vol.%)	Condensate TriEGME Conc. (vol.%)	Test Period (Days)	Pencil Hardness
0	0.006	0.033	-	-	-	3	2H
0.030	0.026	0.031	-	-	-	3	2H
0.047	0.049	0.062	-	-	-	3	H-2H
0.055	0.047	0.077	-	-	-	3	H-2H
0.067	0.067	0.12	-	-	-	3	F-H
0.067	0.069	0.076	-	-	-	5	F-H
0.078	0.076	0.14	-	-	-	3	4B-H
0.100	0.094	0.67	-	-	-	3	<6B-4B
0.101	0.100	0.25	-	-	-	4	<6B-4B
0.140	0.135	0.72	-	-	-	2	<6B
0.156	0.138	1.09	-	-	-	5	<6B
-	-	-	0.051	0.052	0.065	3	2H
-	0.009	0.041	0.080	0.101	0.121	4	2H
-	-	0.02	0.135	0.135	0.15	3	H-2H

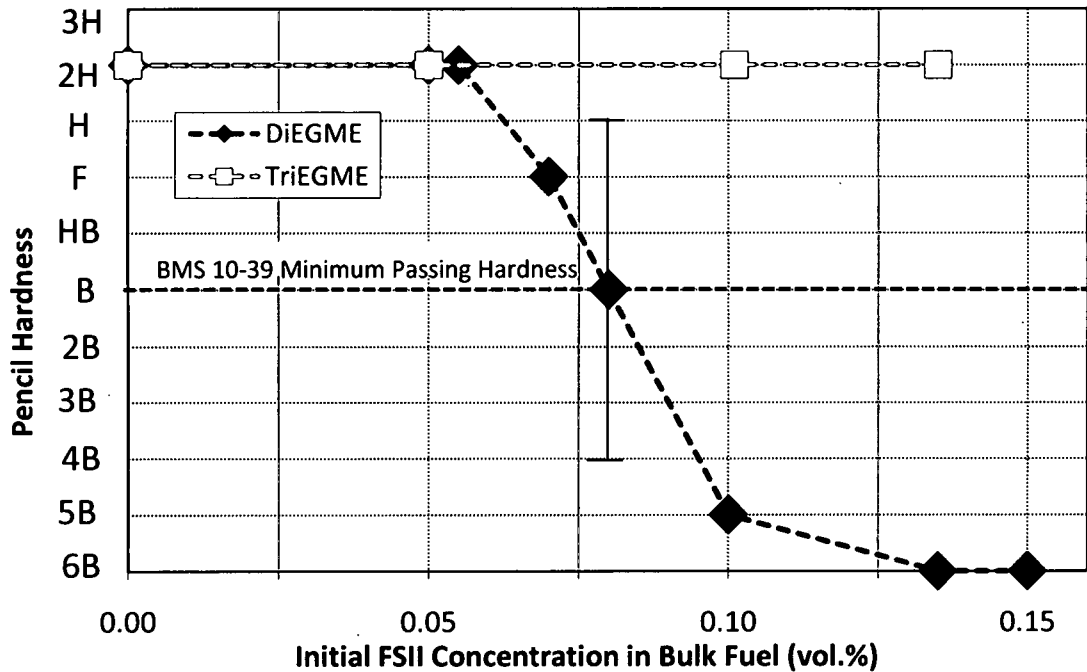


Figure 34: Pencil hardness of older panels after being exposed to varying initial FSII concentrations in the bulk fuel

The degradation of the panels appeared to be evident as three regimes of failure for DiEGME in the bulk fuel. At concentrations below approximately 0.05 vol.% DiEGME initially in the fuel, there were no visible changes in the panel after exposure, and the hardness of the topcoat was unaffected. This is evident by Figure 35, which shows the BMS 10-39 panel exposed to approximately 0.05 vol.% DiEGME initially in the fuel for three days.

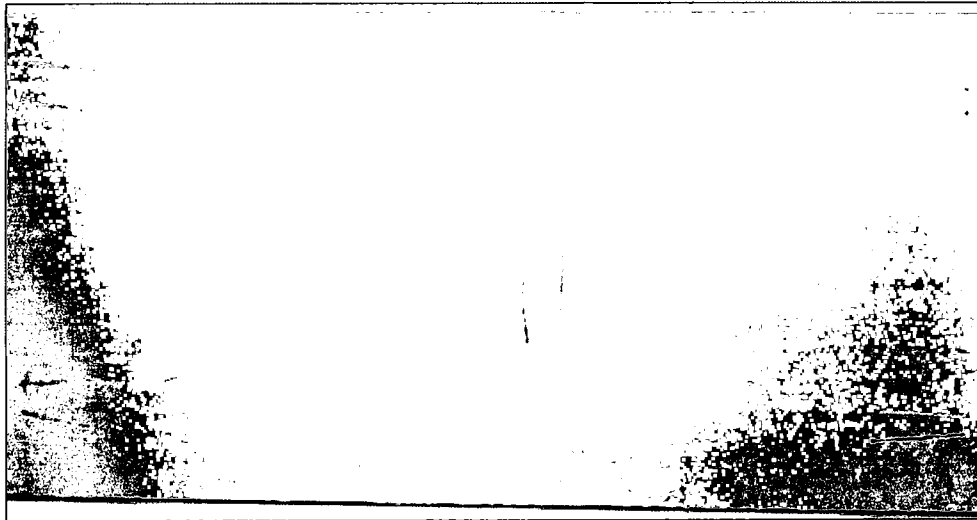


Figure 35: Old panel exposed to approximately 0.05 vol.% DiEGME initially in the bulk fuel

There were no significant changes in visible appearance or hardness of any panels exposed to concentrations in this range. The second regime between approximately 0.05 and 0.10 vol.% DiEGME initially in the fuel showed signs of swelling in the panels. The hardness began to degrade quickly with any further increase in the DiEGME concentration in the fuel, though overall the panels were still relatively intact and did not show any severe signs of swelling and blistering. Figure 36 shows a BMS 10-39 panels after a three day exposure to approximately 0.08 vol.% DiEGME initially in the bulk fuel and the pencil hardness measurements.

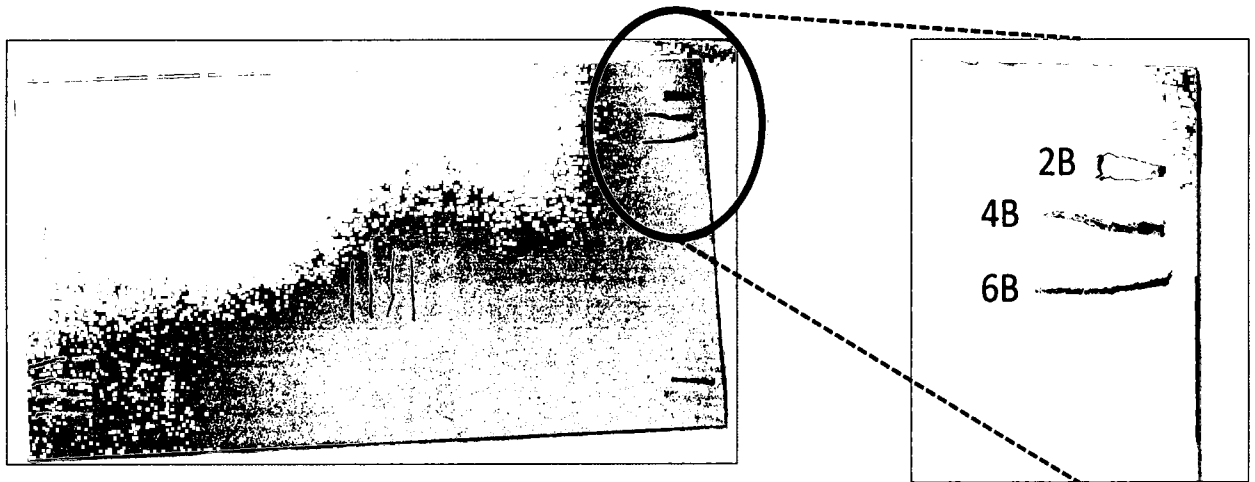


Figure 36: Old BMS 10-39 panel exposed to approximately 0.08 vol.% DiEGME initially in the fuel and the pencil hardness measurements

There were no visible changes in the topcoat panel after exposure to the DiEGME rich condensate; however the hardness of the panel did decrease significantly on some portions of the coating. The center of the panel did pass a hardness of "H," which is within the acceptable range of hardness for BMS 10-39, however the edges only passed at "4B."

A complete failure of the topcoat panels was visible for dose concentrations of approximately 0.10 vol.% DiEGME in the fuel or greater. Along with the hardness decreasing below the minimum specifications, the coating itself exhibited signs of severe swelling and blistering as well as a loss of adhesion to the aluminum substrate. Figure 37 shows a topcoat panel after three days exposure to approximately 0.10 vol.% DiEGME initially in the fuel.



Figure 37: Old panel exposed to 0.10 vol.% DiEGME initially in the bulk fuel

The center of the panel passed a hardness of 4B, while the edges of the panel were not tested, as they were severely swollen and delaminated from the aluminum substrate. The largest failure regions on the panel typically occurred on the sides and edges of the panel, while the center showed slightly less degradation. This could potentially be explained by a non-uniform condensation on the surface of the panel due to the design of the heat exchanger. The panel attached to the cooled steel heat exchanger plate by clamps on the edges and along the top of the panel. This may have provided better contact to the heat exchanger and a colder surface that selectively condensed the FSII rich vapor to these regions.

The use of TriEGME in this FFTP simulation study instead of DiEGME provided completely different results for all aspects of this experiment. BMS 10-39 panels showed no degradation after exposure to TriEGME in the condensate at any of the concentrations tested when attempting to reproduce FFTP. Figure 38 shows a topcoat panel after exposure to approximately 0.10 vol.% TriEGME initially in the bulk fuel.

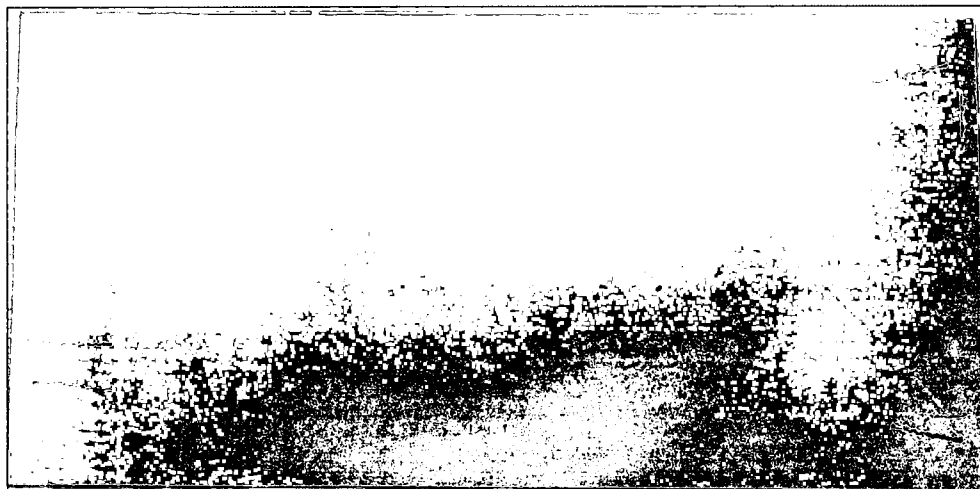


Figure 38: Old panel exposed to 0.10 vol.% TriEGME initially in the bulk fuel

Figure 38 shows a topcoat panel that was completely unaffected by contact with concentrations of approximately 0.12 vol.% TriEGME in the condensate. There is no visible discoloration or swelling after exposure, and the pencil hardness of the coating did not decrease. The panel could potentially be used again in any further experiments as there were no negative effects after contact with TriEGME.

Since both DiEGME and TriEGME performed almost identically in the uptake and pencil hardness testing, the reason for less degradation caused by TriEGME is most likely a lower concentration in contact with the topcoat. This suggests the difference in vapor pressures is able to significantly decrease the concentration of TriEGME in the headspace and subsequent condensate, as supported by the lower TriEGME concentrations in the condensate, discussed further below. Again, this is supported by the study performed by Zabarnick et al. (2007), as the TriEGME concentration in the condensate was well below the DiEGME concentration.

Table 2 shows a large difference between DiEGME and TriEGME with respect to the FSII concentration in the condensate. It should be noted that these FSII concentrations in the condensate are subject to error, as only micro liters were collected from the panel surface. Which such a small quantity of liquid, any increase or decrease

of FSII in the droplets collected would significantly alter the measured concentration. The concentrations of DiEGME in the condensate increased by a factor of up to 7 compared to the initial bulk fuel concentration. Typically, higher concentrations of DiEGME in the fuel yielded much higher concentrations in the condensate. For example, a concentration of approximately 0.15 vol.% DiEGME initially in the fuel resulted in a condensate of 1.09 vol.% DiEGME. TriEGME does not show this large increase in the condensate concentration and only increases by a factor of 1.2 on average for the runs. At a maximum value of 0.15% TriEGME in contact with the topcoat, this is not sufficient to cause degradation, which is also confirmed by the previous pencil hardness study experiments (Figure 31). From the pencil hardness study, the pencil hardness of old panels after exposure to concentrations of 1.0 vol.% DiEGME in the surrogate resulted in a hardness of <6B, which is seen in this study as well. The increase in DiEGME concentrations in the condensate is also supported by the ullage box data obtained from Zabarnick et al. (2007). In Table 2 and Figure 10 (Related Fuel Tank Topcoat Peeling Research), the concentration of DiEGME in the condensate clearly increased from the initial concentration in the fuel for each experimental condition. However, TriEGME differs slightly in these two studies. The data from Table 2 shows an increase of TriEGME in the condensate, while Zabarnick et al. (2007) show a significant decrease in the TriEGME condensate. This difference could potentially be explained by the relatively low distillation percentage collected in the ullage box. Also, the glass collector used in the ullage box condensed the fuel condensate at a much lower temperature of -10°C. This lower temperature would no longer selectively condense TriEGME from the vapor, and would promote other fuel components to condense, lowering the concentration of TriEGME.

Some DiEGME was noticed in the TriEGME runs, and this was believed to be caused by carry over from the tubing used to provide the coolant water for the heat

exchanger. The Viton tubing was sent away for analysis, and was found to have swelled by approximately 1 vol.% due to DiEGME absorption as later analysis showed. Additional experimentation after the tubing was swelled with DiEGME produced trace amounts of DiEGME believed to desorb into the fuel or condensate.

The time needed to reach equilibrium between the vapor, the condensate, and the topcoat was also analyzed from Table 2. Degradation could be seen as early as one day for concentrations of 0.07 vol.% DiEGME or greater in the bulk fuel; however, more time was given to ensure the entire panel reached equilibrium. Figure 39 shows a BMS 10-39 panel clamped to the heat exchanger while exposed to approximately 0.10 vol.% DiEGME after one day.

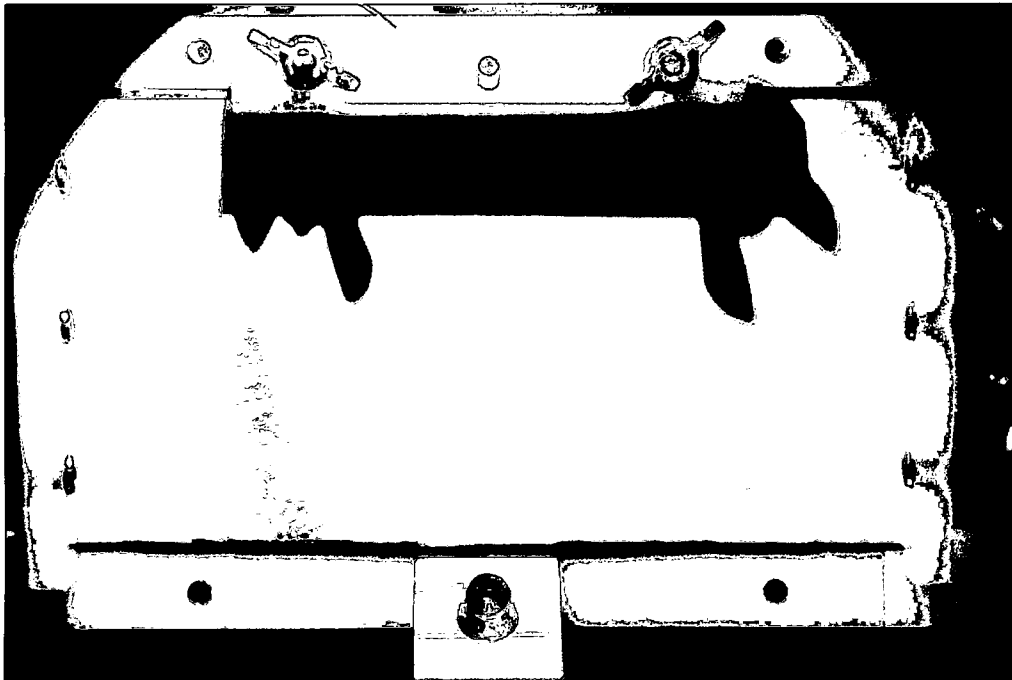


Figure 39: BMS 10-39 panel in the FTTP simulation box showing severe swelling after one day of exposure to approximately 0.10 vol.% DiEGME in the fuel

It is evident there is a large quantity of the FSII rich condensate in contact with the topcoat surface, which has begun to swell and blister because of these conditions. Figure 39 also serves to show the increased condensation on the edges of the panel,

where increased amounts of fluid are present. At most, three days was found to be sufficient in reaching equilibrium as well as for obtaining a visual confirmation of the panels' integrity. This was confirmed by running two experiments at 0.067 vol.% DiEGME initially in the fuel, with one panel being exposed for three days and the other for five days. While there was a slight difference in the DiEGME concentration in the condensate, the pencil hardness and visual appearance of the panels were identical.

The effects of temperature on the degradation process were also studied with the FTTP simulation experiment to assist in determining the conditions necessary for FTTP to occur. Considering that the temperature of the fuel tank walls as well as that of the fuel will almost constantly be changing while either in flight or on the ground, the temperature of the system could play a critical role in FTTP. The temperature of the environmental chamber and the cooling surface were varied to determine how they affected the vaporization and condensation process in FTTP. Further DiEGME experiments also served to evaluate the minimum concentration of DiEGME in the bulk fuel which would no longer produce FTTP. BMS 10-39 panels were evaluated based upon their pencil hardness as a function DiEGME concentration and temperature, as shown in Table 3. The bulk fuel and condensate concentrations were collected for their DiEGME concentration as done above.

Table 3: Multiple DiEGME runs at various temperatures and concentrations (* denotes 2nd aqueous phase concentration)

Fuel Temperature (°C)	Cooling Surface Temperature (°C)	Initial Conc. (vol. %)	Final Conc. (vol. %)	Condensate Conc. (vol. %)	Test Period (days)	Pencil Hardness
60	20	0	0	0	3	H-2H
		0.047	0.049	0.062	3	H-2H
		0.055	0.047	0.077	3	H-2H
		0.067	0.067	0.12	3	F-H
		0.078	0.076	0.14	3	4B-H
		0.100	0.094	0.67	4	<4B
		0.101	0.100	0.25	4	<4B
		0.140	0.135	0.72	2	<6B
		0.156	0.138	1.09	5	<6B
	30	0.070	0.069	0.046	3	H-2H
		0.088	0.087	0.087	3	H-2H
	10	0.070	0.060	0.19(56.4%)*	3	HB-H
		0.109	0.086	0.28(62.5%)*	3	2B-F
50	20	0.072	0.070	0.10	3	H-2H
		0.093	0.091	0.20	14	F-H
	10	0.079	0.072	0.25(57.1%)*	3	H-2H

The environmental chamber was heated to 50 or 60°C, while the cooling surface temperature was kept between 10 and 30°C for this study. These temperatures were used to further simulate the expected conditions in a fuel tank, as well as determine what temperatures will cause the worst degradation. The initial runs at 60°C fuel, 20°C cooling (60/20°C) showed a significant amount of degradation, especially at concentrations greater than 0.10 vol.% DiEGME initially in the fuel. To further investigate the other temperatures, an initial fuel concentration of approximately 0.07 vol.% DiEGME was used as this was within the transition range. This concentration could then be altered based upon the topcoat behavior to further evaluate the effects of temperature.

Increasing the cooling surface to 30°C increased the hardness of the panel compared to a cooling surface of 20°C, for the two tested concentrations of

approximately 0.07 and 0.09 vol.% DiEGME in the bulk fuel. This is most likely due to the surface temperature being high enough such that DiEGME no longer selectively condensed relative to fuel vapors on the panel, and a larger concentration remained in the vapor phase. The condensate samples did contain lower concentrations of DiEGME than was evident in the experiments with a cooling surface of 20°C. Lowering the cooling surface temperature to 10°C also did not promote FTTP as prominently. While increasing the initial DiEGME concentration in the fuel to approximately 0.11 vol.% did reduce the pencil hardness below the minimum passing hardness at this condition, it still was not as severe of a failure as 60/20°C at a similar initial concentration. Lowering the cooling surface to 10°C appeared to promote condensation of two phases on the topcoat panel, an aqueous and a fuel phase. On the topcoat surface it was evident there were two phases, and the collection of the condensate liquid also yielded two phases in the GC vial. The identity of the phases was confirmed by refractive index as well as GC-MS analysis of the composition and DiEGME concentration. With the addition of an aqueous phase on the topcoat surface, this may have provided a slight benefit to the topcoat integrity. DiEGME will ultimately partition at a higher concentration into the water as they are completely miscible. Water may also serve to "stabilize" DiEGME and prevent absorption into the BMS 10-39 panel.

The other runs involved reducing the fuel temperature to 50°C to determine if lowering the temperature would significantly reduce the vaporization of DiEGME. The 50/20°C experiment at approximately 0.07 vol.% DiEGME did not produce any detectable change in the pencil hardness, or any visual evidence of failure. It was unclear if sufficient exposure time was given to reach equilibrium at this lower temperature, as it would require more time to vaporize DiEGME and accumulate sufficient amounts in the topcoat to cause degradation. The second run at a higher

concentration of approximately 0.11 vol.% DiEGME was exposed for 14 days. The BMS 10-39 panel did decrease in pencil hardness slightly, though the coating was still two pencil leads above the minimum passing hardness. This decrease in hardness was most likely a function of the increased concentration of DiEGME in the fuel and subsequent condensate, and not the increased exposure time. Setting the environmental chamber to 50°C reduced the vaporization of DiEGME in the system such that the condensate concentration did not cause a significant decrease in the topcoat hardness or initiate severe swelling. The final run of 50/10°C also did not degrade the topcoat panel. These conditions created two phases on the panel surface, which seemed to indicate that a cooling surface of 10°C was sufficient to condense any water within the system.

Overall, the re-creation of FTTP in the simulated fuel tank provided strong evidence as to the necessary concentrations and temperature to promote this phenomenon. The initial conditions of 60/20°C were ideal for creating a scenario to create FTTP. While alternative temperatures did produce some deterioration of the BMS 10-39 coating, the hardness of the panel was still above the minimum specification. The fuel temperature needs to be sufficient such that high concentrations of DiEGME are vaporized, and the condensing surface needs to be near ambient temperature to selectively condense the FSII. Based upon this study, further use of DiEGME as the FSII additive will require a significant decrease in the maximum concentration, as FTTP will occur at these concentrations if the correct temperature conditions are reached. The highest concentration that did not cause the hardness of the topcoat to fall below the minimum specification was approximately 0.07 vol.% DiEGME. This initial concentration in the bulk fuel resulted in a lower DiEGME concentration in the condensate, which did not cause any significant swelling or blistering of the panel. TriEGME also functioned very well at all of the concentrations tested in this experiment. Because of the lower

vapor pressure of TriEGME, it will not vaporize as readily from the bulk fuel compared to DiEGME. While the TriEGME concentration in the condensate did increase relative to the initial fuel concentration, it was not significant enough to cause failure up to approximately 0.14 vol. %.

CHAPTER IV

CONCLUSIONS AND FUTURE WORK

Conclusions

The material compatibility of DiEGME and TriEGME was explored to provide a better understanding of FTTP as well as analyze the requisite conditions to prevent such phenomenon. Both Fuel System Icing Inhibitors (FSII) additives were found to partition equally on a molar basis into the topcoat with over a wide range of concentrations. This was shown for aqueous, fuel, and the fuel surrogate solutions. The absorption of FSII also increased dramatically if old panels were used instead of new panels for these solutions. The old panels represented a worst-case scenario for FTTP occurring, as they have been exposed to fuel and weather conditions for many years. Newer panels most likely were more resistant to FSII absorption than what is currently present in B-52 aircraft. These two sets of panels were able to represent an expected range of resistance to FTTP.

The desorption rate of FSII out of the topcoat differed between DiEGME and TriEGME. Initially, TriEGME showed a slower desorption rate than DiEGME, which could be explained by its lower vapor pressure and mole size. After two hours, the DiEGME and TriEGME concentrations in the panel began to reach similar levels, and eventually reached a final concentration of approximately 0.66 mol FSII/L TC after aqueous exposures of 80 vol.% FSII or greater. This concentration was similar to that from failed topcoat flakes, which suggested the FSII component in the topcoat will not

completely desorb or evaporate if exposed to high concentrations of FSII. The absorption study data also proved very similar in regards to the Pencil Hardness data, as both DiEGME and TriEGME performed identically within experimental error under the same conditions. The pencil hardness study showed a very large difference between the new and old panels, with the old panels falling below the passing hardness lead of "B" when exposed to FSII concentrations as low as 0.40 vol. % in the fuel surrogate. As the FSII component desorbs from the topcoat, the hardness of the BMS 10-39 coating also begins to increase and maintain the polymer integrity for a larger range of concentrations. This hardening effect proves valuable to preventing FTTP, as higher concentrations which could cause swelling and blistering will not remain in the BMS 10-39 coating for long periods of time.

The developed experimental system that attempted to re-create FTTP in a controlled setting was able to provide valuable information pertaining to the requisite conditions for failure to occur. DiEGME was able to concentrate in the ullage by a factor of 2 to 7 times the initial concentration in the fuel. These higher concentrations in the condensate proved detrimental to the topcoat. The highest concentration in the bulk fuel that did not cause a failure as rated by the penciled hardness of the coating was at approximately 0.07 vol.% DiEGME. However, TriEGME proved very effective in this experiment as it did not lower the pencil hardness of the topcoat panel up to approximately 0.14 vol.% TriEGME initially in the fuel. The resulting TriEGME condensate concentration did increase on average by a factor of 1.2, though this small increase did not prove detrimental to the BMS 10-39 panel. The lower vapor pressure of TriEGME was able to reduce the amount vaporized due to heating the fuel. Based upon these results, TriEGME has been shown to be an adequate FSII replacement in terms of material compatibility. During the scenarios analyzed in these studies, TriEGME would not be believed to cause degradation to the topcoat at the current concentrations of

DiEGME in JP-8. If DiEGME is continued as the FSII, it would be recommended to lower the maximum concentration to at least 0.07 vol.% in the fuel. This could prevent high concentrations of DiEGME vaporizing and condensing on the topcoat surface.

FTTP occurring in the simulated fuel tank box was very depended upon the temperature of the fuel and condensing surface. Fuel temperatures of 60°C were able to vaporize sufficient concentrations of DiEGME to cause swelling and blistering to occur. Lower temperatures were able to vaporize DiEGME; however, the subsequent concentrations in the condensate were not sufficient to cause degradation of the coating. The cooling surface temperature seemed to selectively condense DiEGME at 20°C. If the temperature was higher than this, most likely more DiEGME was maintained in the vapor. As the temperature was dropped below 20°C, other components condensed on the topcoat surface, including water, which decreased the concentration of DiEGME in contact with the polymer.

Future Work

A future study for analyzing the conditions for FTTP may include a more extensive temperature analysis while performing the absorption and pencil hardness studies. Varying temperature while performing these studies would further define the FSII concentrations required to degrade the BMS 10-39 coating. These studies have initially only been performed at ambient temperatures, which does not encompass all the temperatures experienced in the fuel tank. The study could be carried out in an environmental chamber to vary the temperature above or below ambient during the exposures.

Another possibility for a modified study would be to rate the adhesion loss as well as the pencil hardness during the Pencil Hardness and FTTP Simulations studies.

Adhesion of the BMS 10-39 coating to the aluminum is vital for creating a physical barrier to prevent fuel contact with the substrate. It was noted during the previous studies that the topcoat occasionally delaminated from the aluminum during exposure to high concentrations of DiEGME or TriEGME. Evaluating this adhesion loss would provide further evidence of whether or not the topcoat has reached a "critical" failure point. Using ASTM D 3359, "Standard Test Methods for Measuring Adhesion by Tape Test," it would be possible to evaluate the adhesion of the topcoat after exposure to aqueous, fuel, or the fuel surrogate solutions.

Understanding the effects of pressure on FTTP would further determine what conditions promote this phenomenon. Lower pressures are experienced at high altitudes, which are also present in the vented fuel tanks of B-52 aircraft. This will increase the mole fraction of FSII in the vapor, though this lower total pressure is also present at a lower temperature, which will reduce volatilization. It is also reported this lower pressure will increase the mass transfer rate (Aliband et al., 2008). Analysis of the pressure effects could be carried out using the FTTP simulation box with some modifications. The box was designed to hold a vacuum for a given period of time; however, it was not completely leak-free. Once the lid is vacuum-tight, the FTTP simulation could be repeated at lower or even possibly higher pressures to determine how pressure affects the hardness of the panel and the FSII concentration in the condensate.

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