

# **Aspects of Epoxy Paint Failure in B-52 Fuel Tanks: Subsequent Oxidation of Aluminum under Aqueous Solutions Containing Fuel System Icing Inhibitor**

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## Abstract

It has been determined previously that paint failure on lower vertical surfaces in B-52 integral wing fuel tanks is due to exposure of the BMS10-32 epoxy protective topcoat to mixtures of water and diethylene glycol monomethyl ether (DIEGME). Upon removal of the topcoat, the exposed aluminum surface is exposed to this aqueous solution. In this communication, a high surface area oxidation prone aluminum model system is developed and used to gain preliminary insight into the oxidation of bare 2024-T351 and 7075-T651 aluminum alloys upon exposure to aqueous solvents containing diols, monoalkyl ethers, and dialkyl ethers based on ethylene glycol. These preliminary experiments reveal an alternate fuel system deicing additive that appears to passivate 2024-T351 and 7075-T651 aluminum towards oxidation under aqueous solutions containing the additive.

## Key words and phrases

**JP-8, B-52, aluminum, corrosion, EGME, DIEGME, TRIEGME**

## Introduction

Small amounts of the protective polyamine – epoxy topcoat in B-52 integral wing fuel tanks have failed and debonded from the aluminum wingskin. Exfoliated paint is removed during routine maintenance. In Part I of a series in “Journal of Organic Coatings”<sup>(1)</sup> models were proposed to account for paint failure on upper vertical surfaces in the fuel tank, and for paint failure on lower horizontal surfaces in the fuel tank. These models were validated by experimental testing. In Part II of this series<sup>(2)</sup>, more sophisticated tests were devised in support of the model used to explain failure on upper vertical surfaces in the fuel tank. Paint failure on upper vertical surfaces is due to interaction of the paint with condensed distillates from JP-8 (kerosene based) military jet fuel that are enriched with diethylene glycol monomethyl ether (DIEGME) – the fuel system icing inhibitor (and plasticizer of BMS10-39 paint) used in most military aviation systems worldwide. On the basis of these tests<sup>(2)</sup>, it was concluded that failure on upper vertical surfaces could be reduced by reducing the level of DIEGME fuel system icing inhibitor (FSII) in the JP-8 jet fuel.

In contrast, paint failure on the floor of the fuel tank is due to interaction of the paint with solutions of diethylene glycol monomethyl ether (DIEGME) in water that form as the DIEGME is extracted out of the fuel into pools of water that form on the floor of the fuel tank. The BMS10-39 polyamine – epoxy topcoat is used primarily as a corrosion barrier in the fuel tank. Therefore, concerns have been raised as to the possibility of subsequent corrosion of the underlying aluminum in contact with aqueous sump fluid containing fuel system deicer..

The B-52 wingskin is manufactured from 2024-T351 aluminum. Internal stiffeners are manufactured from 7075-T651 aluminum. The elemental composition of both alloys is given

in **Table 1(a)**. Selected mechanical properties are given in **Table 1(b)**. Aluminum 7075-T651 is the stronger alloy. Aluminum 2024-T351 is the more ductile alloy. Both alloys are susceptible to corrosion and are protected in the B-52 fuel tank by a conversion coating under the BMS10-39 paint.

**Table 1.** (a). Elemental composition of 2024-T351 and 7075-T651 aluminum (b). Physical properties of 2024-T351 and 7075-T651 aluminum (c). % weight gain of activated millings of aluminum 2024-T351 and 7075-T651 after 90 days exposure at 35°C to distilled water and salt solution (d). Composition of salt solution

Aluminum alloy	2024-T351	7075-T651
(a). Wt.% Composition (ASM data sheet)	Al 90.7 – 94.7 % Zn 0.25 % Mg 1.2 – 1.8 % Cu 3.8 – 4.9 % Cr 0.1 % max Fe 0.5 % max Si 0.5 % max Mn 0.3 – 0.9 % Ti 0.15 % max	Al 87.1 - 91.4 % Zn 5.1 – 6.1 % Mg 2.1 - 2.9 % Cu 1.2 – 2.0 % Cr 0.18 – 0.28 % Fe 0.5 % max Si 0.4 % max Mn 0.3 % max Ti 0.2 % max
(b). Tensile yield strength Elongation at break (ASM data sheet)	324 MPa 20 %	503 MPa 11%
(c). % Wt. gain in distilled water % Wt. gain in salt solution*	23.3 80.4	24.3 102.6
(d). *Composition of representative salt solution	NaCl NaF CaCl <sub>2</sub> KNO <sub>3</sub> Na <sub>2</sub> SO <sub>4</sub> (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> K <sub>2</sub> PO <sub>4</sub> H	2.050 X 10 <sup>-2</sup> g/L 3.360 X 10 <sup>-2</sup> g/L 1.110 X 10 <sup>-2</sup> g/L 1.520 X 10 <sup>-2</sup> g/L 0.380 X 10 <sup>-2</sup> g/L 0.920 X 10 <sup>-2</sup> g/L 0.260 X 10 <sup>-2</sup> g/L

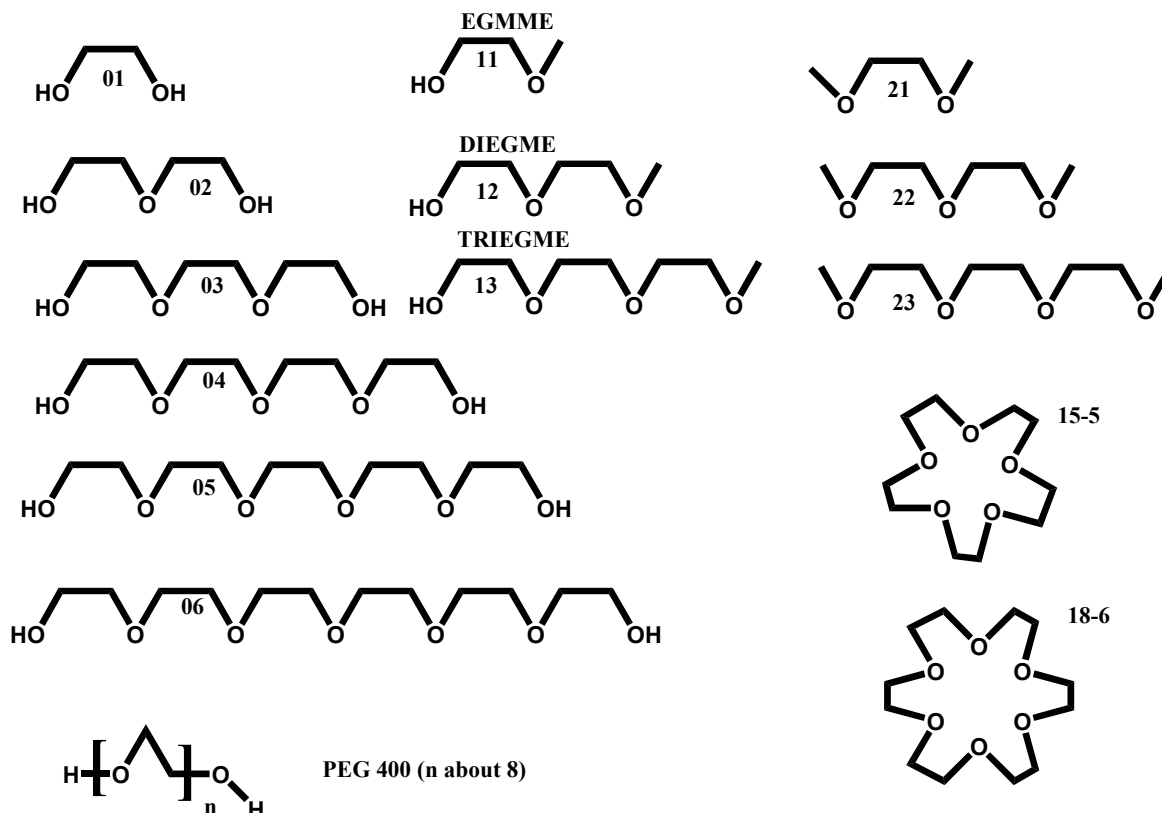
Prior to application of the epoxy topcoat, all aluminum substrates in the B-52 fuel tank were treated with Alodine 1200, a chromium (VI) containing conversion coating formulated

to enhance subsequent adhesion of the paint and provide corrosion protection<sup>(3)</sup>. The complete absence of any visual signs of corrosion on exposed aluminum is attributed to the conversion coating that is still observable on the surface of the aluminum. Although corrosion of the underlying aluminum is not observed, the adoption of a proactive stance requires that certain hypothetical questions be asked, and that attempts be made to arrive at answers. For example, although an enormous effort has been made to understand the corrosion of aluminum alloys of interest to the aviation industry, in water and in aqueous electrolyte solutions<sup>(4-7)</sup>, little is known about the corrosion of aluminum under solutions of DIEGME in water. In addition, if the rates of corrosion under mixtures of water and DIEGME are benchmarked, could corrosion be reduced if the DIEGME were replaced by another fuel system deicing additive? It is the purpose of this communication to begin to answer these questions.

The initial goal of this work was to gain some preliminary insight into how bare aluminum on the floor of the B-52 integral wing fuel tank will oxidize under aqueous solutions containing diethylene glycol monomethyl ether (DIEGME), if the aluminum had not been passivated towards oxidation by the Alodine 1200 conversion coating.

In order to view these results within a broader context, other compounds based on ethylene glycol were also tested. Compounds used to generate the test matrix are labeled and sketched in **Figure 1**. Compounds tested included diol terminated ethylene glycol (EG) based oligomers ("0x"), ethylene glycol based oligomers terminated with one hydroxyl group and one methyl ether group ("1x"), and ethylene glycol based oligomers terminated with two methyl ether groups ("2x"), where 0,1, or 2 refers to the number of terminal methyl ethers in the compound and x refers to the number of ethylene glycol residues in the compound. For example, using this shorthand, triethylene glycol monomethyl ether or TRIEGME is labeled compound 13 in **Figure 1**. Cyclic crown ethers 15-5 and 18-6 were also tested.

It has been determined previously<sup>(1)</sup> that an aqueous sump solution must contain a minimum of about 50% DIEGME in order to remove the protective epoxy topcoat. Sump solutions containing up to 50% DIEGME have been recovered during routine maintenance. The content of DIEGME and other EG based compounds in the test solution was, therefore, set at 50 volume %.



**Figure 1.** Compounds based on ethylene glycol: Nomenclature for convenience (ab) with a = # of methyl ether end groups & b = # of ethylene glycol units. (For example, using this shorthand, diethylene glycol monomethyl ether is represented as compound 12)

## Materials and Methods

### Aluminum millings

Aluminum millings were cut from blocks of 2024-T351 aluminum and 7075-T651 aluminum.

A new tool was used and the top layer of aluminum was cut from the block and discarded before collecting sample.

Mill settings are summarized as...

*4000 RPM, 8.0 feed = 0.0005 per tooth, 0.050 step over, 4FLT Ruff Inc., End Mill 3/8" Dia.*

### Reagents

“Deionized water” was purified by reverse osmosis then passage through an ion exchange column and had a conductivity less than  $10^{-5}$  s/m. Solvents were reagent grade or better.

Compounds based on ethylene glycol were purchased from national supply houses, all 97% pure or better, and were used as received.

### Sample Preparation and Optical Microscopy

Aluminum millings were exposed to an excess of distilled water or other aqueous mixture in a sealed test tube (for example – 100mg Al under 10 ml solution). Each day thereafter, the millings were agitated gently and a small portion were carefully transferred to a test tube containing tetrahydrofuran (THF) solvent to remove water and additive, then to a thick pad of absorbent paper. After repeated rinsing with THF onto and through the paper then evaporation of the THF solvent, the millings were carefully transferred to the microscope for examination. Digital images were recorded using a Nikon Koolpix 8700, 8Mpx digital

camera mounted on a Reichart Microstar IV optical microscope, using an aftermarket adaptor from “Microscope World”. All photographs were recorded at a magnification “X10”. Using a calibrated slide, the long axes of all photographs were determined to be approximately 1.28 mm.

## **Sample Preparation and the Long Term Oxidation (LTO) Experiment**

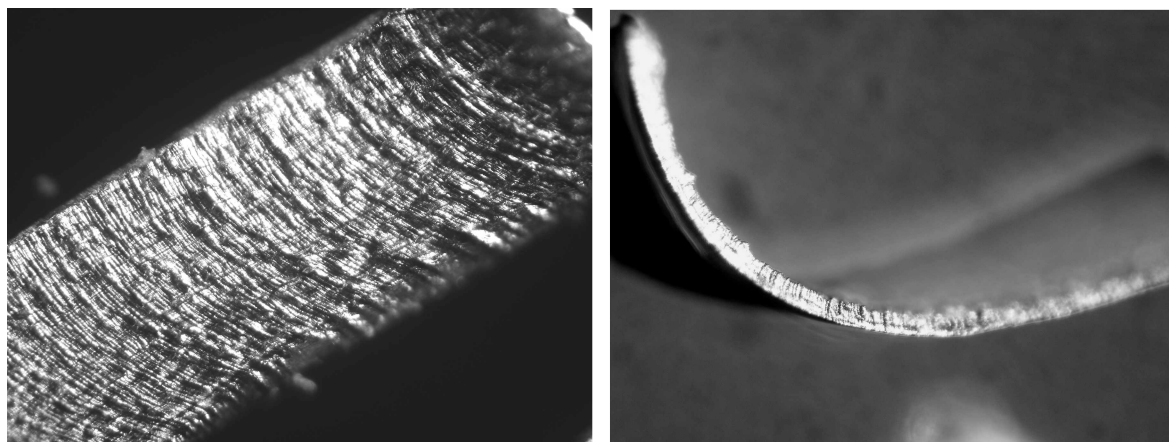
The sample consisted of approximately 2g (measured to 3 decimal places) of 2024-T351 or 7075-T651 aluminum millings in a Teflon gasketed screw top test tube. Aqueous solutions recovered from B-52 fuel tanks during routine maintenance have been shown to contain up to 50% by volume of DIEGME. As such, and for want of a better imperative, soak solution were made to consist of 50% by volume of organic compound + 50% by volume of distilled water or salt solution, the composition of which is detailed in **Table1(d)**. Samples were held at  $35 \pm 1^\circ\text{C}$  for 90 days in a forced air oven with digital controller, and were agitated every 7 days using a vortex mixer. At the end of the LTO experiment, liquid was decanted off, distilled water was added, the residue was agitated, and liquid was removed. This was repeated a minimum of 3 times, then the sample was washed with tetrahydrofuran (THF) 4 times. In some instances, the flakes had fused and had to be physically separated to allow for efficient washing. In some instances, the container had to be left for some time to allow colloidal aluminum oxide to settle before the mother liquor was decanted out of the tube. The washed aluminum residue was “dried” in a forced air oven at  $90^\circ\text{C}$ , then in a vacuum oven at  $50^\circ\text{C}$  before re-weighing.



## Results & Discussion

Aircraft fuel tank sump fluid can promote microbial growth, and microbial growth can promote corrosion by changing pH and producing redox active compounds<sup>(8)</sup>. Therefore, the composition of fuel tank sump fluid in B-52 and related aircraft has been surveyed in the context of a broader program of work designed to gain understanding of the ecology of microbial and fungal growth in these fuel tanks<sup>(9)</sup>. From this work, a consensus was reached by the U.S. Air Force into the composition of a “representative” salt solution, as detailed in the Materials and Methods section. Test solutions were put together using either distilled water or this representative (very dilute) salt solution.

A second, and perhaps more important, goal of this work was to identify potential anti-icing additives that can passivate the aluminum surface towards oxidation in aqueous solution. To amplify differences between additives, a highly reactive aluminum model system had to be devised. The simplest way to activate aluminum towards oxidation is to increase specific surface area by reducing particle size. High surface area aluminum, sufficiently reactive to be classified as a fire hazard, may be purchased from any chemical supply house. However, the oxidation of aluminum is also profoundly influenced by the inclusion of small amounts of other elements. **Table 1(a)** contains a compositional breakdown of aluminum 2024-T351 and 7075-T651. Aluminum 2024-T351 is classified as a high copper alloy and aluminum 7075-T651 as a high zinc alloy. Any model system had to reflect compositional differences between the two alloys. An alternative way to activate aluminum towards oxidation is to generate a high concentration of surface cracks, and other defects<sup>(4-6)</sup>. This was achieved by milling flakes from an aluminum block, without the use of lubricant, using a programmable tool. Milling parameters are reproduced in the Materials and Methods section.



**Figure 2.** Optical microscopy of milled flakes of 7075 aluminum (X10) **(left)** showing length and breadth **(right)** in cross section. The long axis of both photographs  $\sim 1.28$  mm.

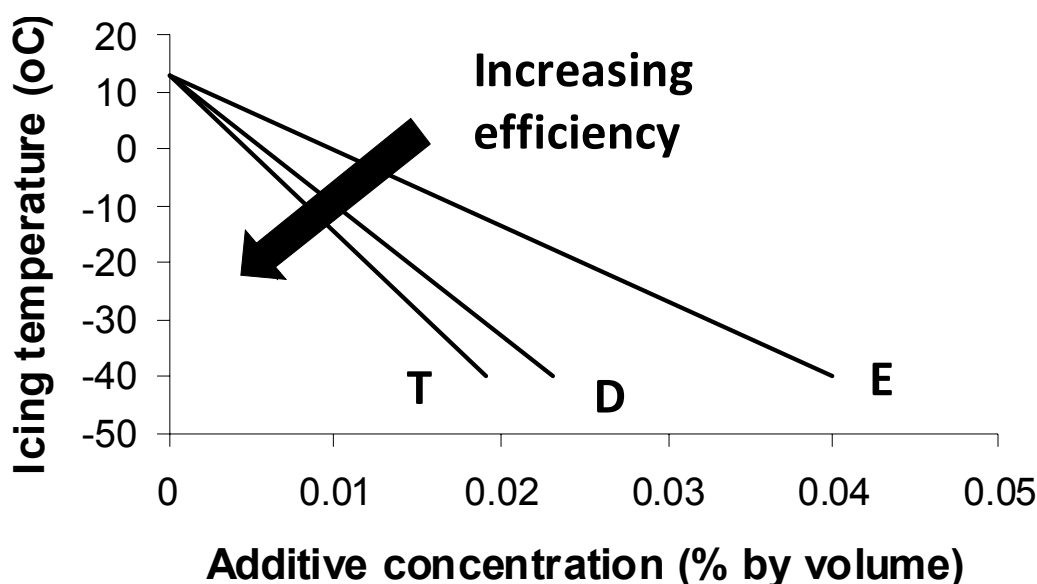
Millings from blocks of 2024-T351 and 7075-T651 aluminum, produced by this method, were uniform in size and thickness. The high concentration of surface defects introduced by cold working the aluminum in this fashion are illustrated in **Figure 2 (left)**. The high aspect ratio of these millings is illustrated in **Figure 2 (right)**, from which it may be observed that “surface” defects appear to occupy a significant volume fraction of the milling. By microscopy, the average dimensions of an aluminum flake of both alloys (neglecting surface roughness and flaws) was calculated to be around  $1.95\text{mm} \times 0.65\text{mm} \times 40\mu\text{m}$  thick, or  $\approx 200 \text{ cm}^2/\text{g}$  of aluminum.

It must be noted that the major purpose of the long term oxidation experiments was to identify compounds that suppress oxidation of the aluminum alloys. To this end, experiments were performed under conditions that led to excessive amounts of oxidation in some other systems. Physical changes that accompany oxidation in these excessively oxidized samples can influence the rate of further oxidation (clumping, fusing, etc). Therefore, no attempt was made to contrast reactivity in these more reactive systems.

## Optical Microscopy of the Aluminum Model System

As a preliminary to the long term oxidation experiments, the initial development of oxidation on millings of the 7075-T651 aluminum model system, on a shorter time scale of days, was recorded as a function of time using optical microscopy. Aluminum 7075-T651 is, in general, less susceptible to corrosion than aluminum 2024-T351, due to the lower level of copper in the alloy. By using aluminum 7075-T651 in these experiments, it was assumed that the rate of corrosion would be slower and differences between additives would be accentuated. Sample preparation and handling are detailed in the Materials and Methods section. Soak solutions included distilled water (DW) and 50/50 by volume mixtures of distilled water and the three readily available monomethyl ether derivatives of ethylene glycol. The first - ethylene glycol monomethyl ether or EGME (compound 11 in **Figure 1**) had been used in JP-8 fuel until it was found to be a health hazard. The second – diethylene glycol monomethyl ether or DIEGME (compound 12 in **Figure 1**) is the deicing additive currently added to JP-5 and JP-8 military jet fuel. DIEGME is somewhat less toxic than EGME,<sup>(10)</sup> and is a more effective fuel system icing inhibitor (FSII) than EGME.<sup>(11)</sup> (Other less toxic, non EG based FSII compounds have been synthesized and evaluated,<sup>(12)</sup> but have not yet been adopted commercially). The third compound – triethylene glycol monomethyl ether or TRIEGME (compound 13 in **Figure 1**) has also been evaluated in the laboratory as a deicing additive in military jet fuel<sup>(13)</sup>, but has never been used as such in the field. The relative effectiveness of EGME, DIEGME, and TRIEGME as FSII is illustrated in **Figure 3**, constructed using data abstracted from published Navy research<sup>(13)</sup> on the three compounds. To achieve a fixed sub-ambient icing temperature the required level of DIEGME and TRIEGME in the fuel is approximately 58% and 47% respectively of the required level of

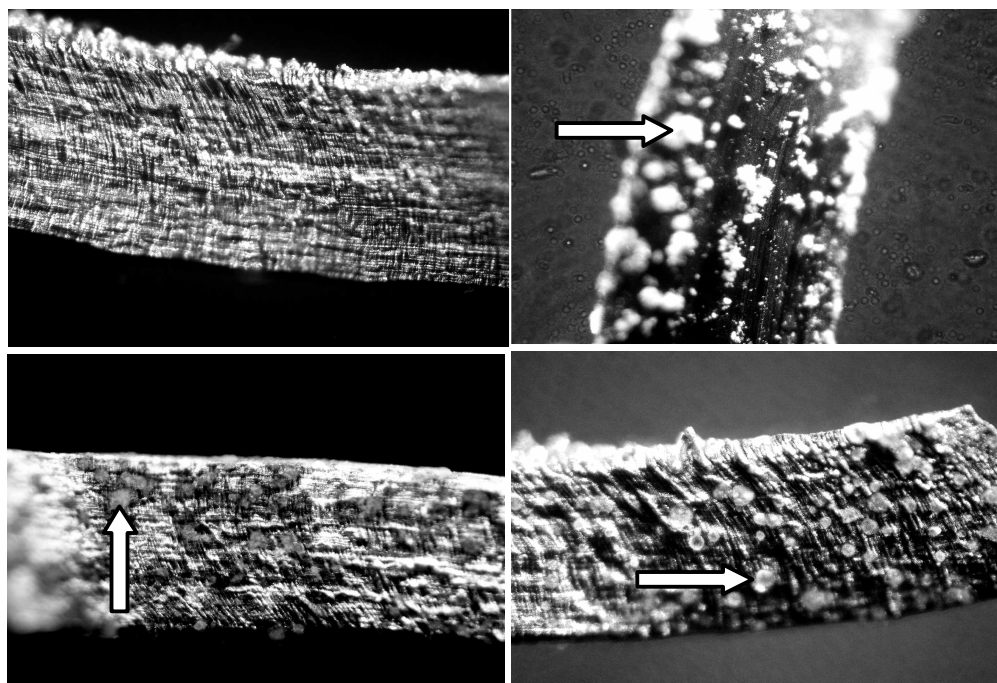
EGME. In other words, TRIEGME is the most efficient FSII while EGME is the least efficient FSII.



**Figure 3.** Plot of icing temperature vs additive concentration for EGME, DIEGME, and TRIEGME [replotted from published US Navy research<sup>(13)</sup>]

The first appearance of surface oxidation on millings of 7075-T651 aluminum, on storage under these soak solutions, is illustrated in **Figure 4**. A photograph of unoxidized 7075-T651 aluminum is inserted (**Figure 4, top left**) for comparison. After 1 day under distilled water (**Figure 4, top right**), millings of 7075-T651 aluminum are completely coated with a thick oxidized layer. After 3 days under a 50/50 by volume mixture of distilled water and EGME (**Figure 4, bottom right**), isolated pockets of translucent aluminum oxide (arrowed) are observed to be growing from the surface of the aluminum. After 15 days under a 50/50 by volume mixture of distilled water and DIEGME (**Figure 4, bottom left**), isolated

pockets of translucent aluminum oxide (arrowed) are observed to be growing from the surface of the aluminum flakes.

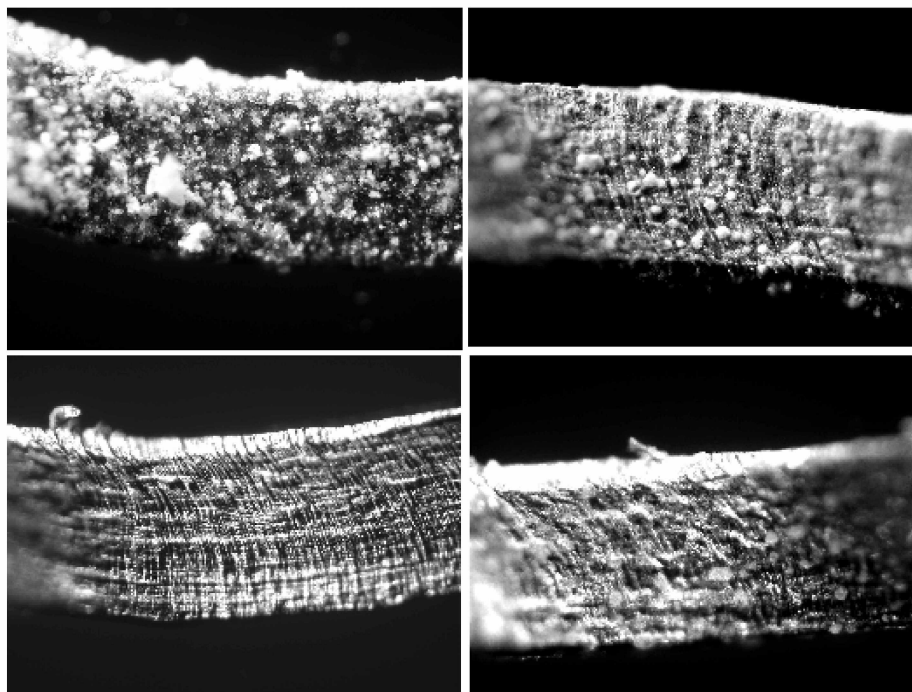


**Figure 4.** First appearance of oxidation by optical microscopy (**Top left**) Unaltered 7075-T651 aluminum millings for comparison (**Top right**) 7075-T651 aluminum millings after 1 day in distilled water (**Bottom right**) 7075-T651 aluminum millings after 3 days in distilled water + 50 volume % EGMM (**Bottom left**) 7075-T651 aluminum millings after 15 days in distilled water + 50 volume % DIEGME. The long axis of all photographs ~ 1.28 mm.

The experiment was terminated after 21 days. The fate of 7075-T651 aluminum millings after 21 days exposure to the four soak solutions is illustrated in **Figure 5**. Aluminum millings under distilled water are oxidized massively after 1 day (**Figure 4, top right**) and are little altered after 21 days exposure (**Figure 5, top left**). The extent of oxidation of 7075-T651 aluminum after 21 days under 50/50 by volume solutions of distilled water and, either of, EGME (**Figure 5, top right**) or DIEGME (**Figure 5, bottom right**) has advanced over that initially detected after 3 days and 15 days respectively. In contrast,



millings of 7075-T651 aluminum that are exposed to a 50/50 by volume solution of distilled water and TRIEGME for 21 days (**Figure 5, bottom left**) show *no visual signs of oxidation*.



**Figure 5.** Photographs of activated millings of 7075-T651 aluminum (all X10) after 21 days exposure to **(top left)** distilled water **(top right)** distilled water + 50 volume % EGME **(bottom right)** distilled water + 50 volume % DIEGME **(bottom left)** distilled water + 50 volume % TRIEGME. The long axis of all photographs ~ 1.28 mm.

The results of these preliminary qualitative experiments may be summarized as follows. First of all, 7075-T651 aluminum millings are activated towards oxidation in distilled water, with massive thick oxide coverage observed after only 1 day exposure to distilled water. Secondly, the initial onset of visually observable oxidation is delayed to 3 days when EGME is added to the distilled water, and to 15 days when DIEGME is added to the distilled water. The subsequent rate of buildup of oxidation thereafter under solutions containing EGME and DIEGME is further delayed. EGME and DIEGME appear to retard the development of oxidation on 7075-T651 alloy, with DIEGME as the more active of the two.

Oxidation of the aluminum is not observed after 21 days under a 50/50 by volume solution of distilled water and TRIEGME. Subsequent long term oxidation (LTO) experiments will reveal that solutions of TRIEGME in distilled water or salt solution appear to passivate both aluminum 2024-T351 and 7075-T651 surfaces towards oxidation over a much longer time interval.

### Long Term Oxidation (LTO) Experiment

Experiments were performed over a longer timescale in order to better compare and contrast the influence of ethylene glycol derivatives on the oxidation of 2024-T351 and 7075-T651 aluminum. The presence of the additive in the soak solution reduces the solubility of products of oxidation in that solution. The level of oxidation was, therefore, measured as the weight **gained** by the sample. Samples were prepared and aged as outlined in the Materials and Methods section.

At short times, in distilled water, salt solution, and in solutions containing ethylene glycol (EG) derivatives that do not passivate the aluminum, the oxidation reaction was sufficiently fast that bubbles of hydrogen were seen to percolate out of the solution. A number of instances were observed in which clumps of millings were pushed out of solution due to rapid gas evolution. Those solutions were swirled to settle the aluminum and returned to the oven. Evolved hydrogen could not be contained and diffused out of the container. The Teflon<sup>tm</sup> gaskets were, however, sufficiently effective that solution volumes remained relatively stable. Only the most volatile additives (for example “glyme” or 21) were able to escape. The maximum loss of liquid observed in any sample was about 20 volume%. Losses of storage fluid were not made up by adding extra fluid.

Three groups of ether based additives were investigated – diols, monomethyl ethers, and dimethyl ethers, all based on ethylene glycol (**Figure 1**).

- Results are reported for the diols and dimethyl ethers in distilled water. Those additives that completely passivate the aluminum as mixtures with distilled water, also completely passivated the aluminum when mixed with salt solution.
- For other additives, the extent of oxidation of the aluminum under mixtures of the additive with salt solution was greater than the extent of oxidation of the aluminum under mixtures of the additive with distilled water.
- Results are reported also for oxidation of the aluminum under solutions of the monomethyl ether additives with both distilled water and salt solution.

### **Oxidation of Aluminum Alloy under Distilled Water and Salt Solution**

The % weight gain of 7075-T651 and 2024-T351 aluminum alloys after 90 days exposure to distilled water and salt solution at 35°C, is summarized in **Table 1(c)**. The weight gained by 7075-T651 alloy in distilled water (24.3%) is marginally higher than the weight gained by 2024-T351 alloy in distilled water (23.3%). The extent of oxidation of both alloys in salt solution is massively higher than in distilled water. The end product will be a mixture of the many forms of hydrated aluminum oxide  $[Al_2O_3 \cdot xH_2O]$  – Gibbsite, Bayerite, etc.<sup>(14)</sup>



## Oxidation Under Aqueous Solutions Containing Diols Based on Ethylene Glycol

### Glycol

The oxidation of 2024-T351 and 7075-T651 aluminum under mixtures of diol derivatives based on ethylene glycol (compounds designated 01 – 06 & PEG400 in **Figure 1**) with distilled water and salt solution, was performed as outlined earlier in this communication. Sample vials containing aluminum 2024-T351 after 90 days @ 35°C, under mixtures of the diol compounds with distilled water, are photographed in **Figure 6**.



**Figure 6.** 2024-T351 activated aluminum millings exposed 90 days at 35°C to (from left): Distilled water (DW), then 50/50 by volume mixtures of distilled water and ethylene glycol (01), diethylene glycol (02), triethylene glycol (03), tetraethylene glycol (04), pentaethylene glycol (05), hexaethylene glycol (06), polyethylene glycol (PEG400), JP-8 jet fuel.

Aluminum stored under distilled water (far left) has darkened significantly and fused into a solid mass. Aluminum under solutions of distilled water containing ethylene glycol (01), diethylene glycol (02), and triethylene glycol (03), appear visually to be progressively less oxidized. Aluminum under tetraethylene glycol (04) and higher oligomers appears visually to be free of oxidation (as is aluminum stored under JP-8 fuel under the same conditions, and for the same time, and included for comparison). The volume occupied by the aluminum metal appears to track also the extent of oxidation (Volume under DW > DW/01 > DW/02 > DW/03 > DW/04 ~ DW/05, DW/06, DW/PEG400), although changes in sample morphology that accompany oxidation make this a less than quantitative measure of the extent of reaction.

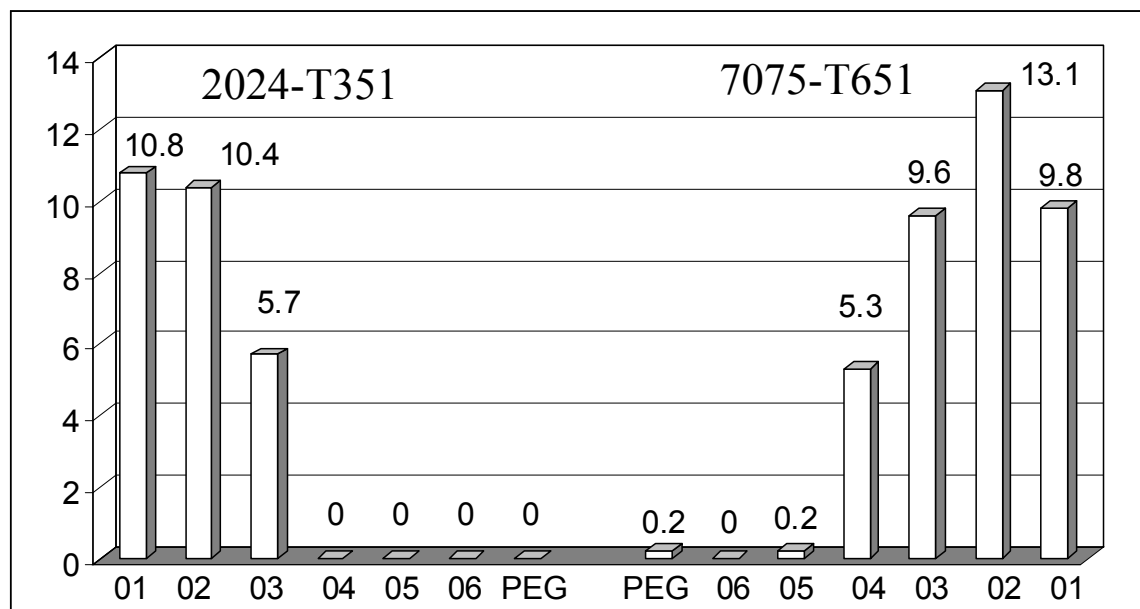
A better estimate of the extent of oxidation is made by measuring the weight gained by the aluminum during the experiment. Sample masses before ( $w_b$ ) and after ( $w_a$ ) oxidation were obtained using the procedure outlined in the Materials and Methods section. The % weight gain was estimated as  $(w_a - w_b) \times 100/w_b$ .

Experimental results are summarized in **Figure 7**. With reference to the results of **Table 1**, it becomes apparent, that oxidation of the aluminum alloys in aqueous solution is reduced in the presence of diols based on ethylene glycol. Most importantly, oxidation appears to be completely suppressed in 2024-T351 alloy upon addition of the tetramer and higher oligomers to the aqueous soak solution (**Figure 7, left**). The oxidation of 7075-T651 alloy is suppressed in the presence of the pentamer and higher oligomers (**Figure 7, right**).

It is well known that the overall ability of an oligomer – polymer to deposit from solution and bind and spread over a surface increases with the molecular weight of the compound, or perhaps more correctly, with the number of binding sites in the compound<sup>(15)</sup>.

Each of these diol compounds possesses two hydroxyl groups available to bind to a polar

surface. In addition, the number of alkyl ether sites available for bonding increases from zero in compound 01 to one in compound 02, two in compound 03, etc... as the diol chain length increases from compound 01 to PEG400. The creation of an adsorbed diol monolayer on the surface of the aluminum should restrict access of water to the surface and, presumably, slow

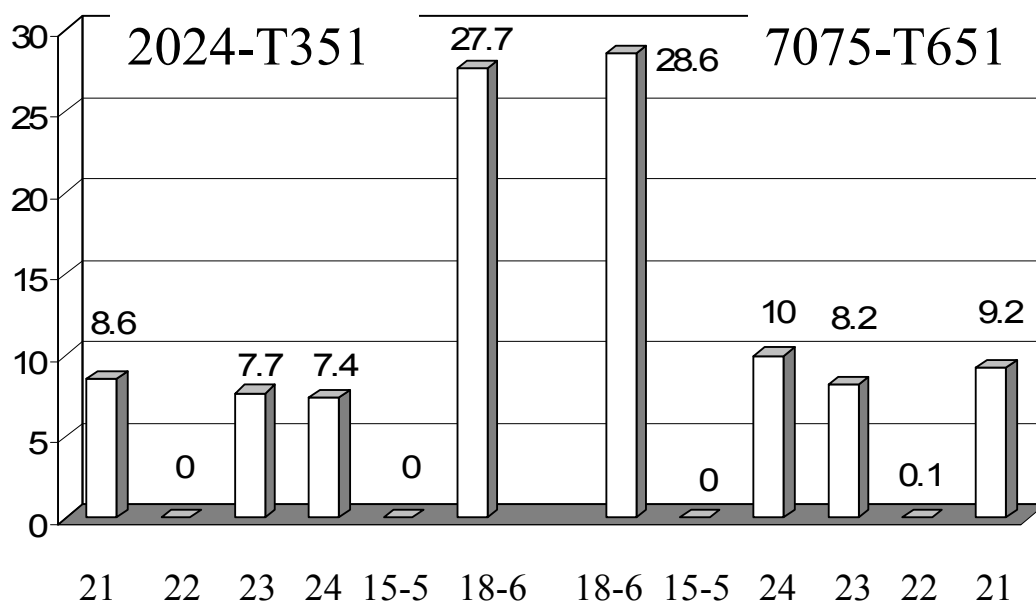


down the rate of oxidation of the aluminum more efficiently at higher diol molecular weights, as is found here<sup>(15)</sup>.

**Figure 7.** Oxidation of activated aluminum millings for 90 days at 35°C in 50 volume % mixtures of distilled water with diols based on ethylene glycol. X axis – compound (see **Figure 1** for structures), Y axis - % weight gain (**left**) 2024-T351 aluminum, (**right**) 7075-T651 aluminum.

## Oxidation Under Aqueous Solutions Containing Dialkyl Ethers Based on Ethylene Glycol

The influence of dimethyl ether end capped derivatives of ethylene glycol on the oxidation of 2025-T351 and 7075-T651 aluminum was ascertained using methods outlined in the previous section. Compounds evaluated are sketched in the extreme right hand column of **Figure 1**, and include the dimethyl ether, of ethylene glycol (compound 21 or “glyme”), of diethylene glycol (compound 22 or “diglyme”), and of triethylene glycol (compound 23 or “triglyme”). Crown ethers 15-5 and 18-6 were included in the test matrix for comparison with the linear compounds. The results of gravimetric experiments are summarized in **Figure 8**.



**Figure 8.** Oxidation of activated aluminum millings for 90 days at 35°C in 50 volume % mixtures of distilled water with diethers based on ethylene glycol. X axis – compound (see **Figure 1** for structures), Y axis - % weight gain (**left**) 2024-T351 aluminum (**right**) 7075-T651 aluminum.

Trends in the influence of the diol compounds, examined previously, on the oxidation of aluminum alloys, can be explained on a purely molecular weight basis. As the chain length of the compound increases, more compound is adsorbed onto the surface and more water is displaced from the surface. Lacking access to water, the oxidation reaction is presumed to be retarded.

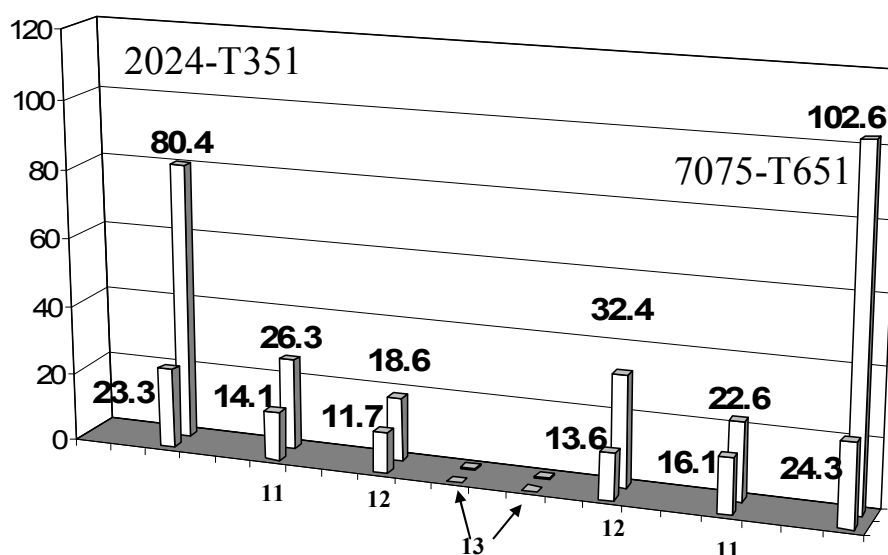
In contrast, some more interesting specific chemical interactions are seen to dominate the oxidation of both aluminum alloys under aqueous solutions containing these wholly methylated glycol ethers. Using weight gain under distilled water as a benchmark (**Table 1(c)**), it is noted that the addition to the soak solution of the linear dimethyl ether derivatives of ethylene glycol, labeled 21 – 24 in **Figure 8**, all lead to a reduced oxidation of both aluminum alloys. Compound 22 (“diglyme”) appears to be unique within this series, in that its addition to the soak solution leads to a complete suppression of oxidation of both aluminum alloys over this time interval, presumably due to specific chemical and/or physical interactions with the aluminum or aluminum oxide surface.

In similar fashion, the addition of crown ether 18-6 to distilled water promotes oxidation of both alloys over that observed even in distilled water, while the addition of crown ether 15-5 completely suppresses oxidation and weight gain. Both compounds are expected to adsorb efficiently onto the aluminum or aluminum oxide surface. The only real difference between the two compounds is in the size of the internal cavity<sup>(16-18)</sup>. The cavity in crown ether 15-5 is sized to complex efficiently with sodium ions, while the cavity in crown ether 18-6 is sized to complex efficiently with potassium ions. The mechanism(s) by which crown ether 15-5 passivates the surface of both alloys while crown ether 18-6 activates the surface of both alloys towards corrosion is beyond the scope of this present discussion but deserves further study.

## Oxidation Under Aqueous Solutions Containing Monomethyl Ethers

### Based on Ethylene Glycol

The influence of the three monomethyl ethers (EGME, DIEGME, and TRIEGME or compounds 11, 12, and 13 respectively in **Figure 1**) on the oxidation of aluminum 7075-T651, was examined previously by optical microscopy at short times. The influence of these three FSII compounds on the oxidation of 2024-T351 and 7075-T651 aluminum in aqueous solution at longer times was re-examined.



**Figure 9.** Oxidation of activated aluminum millings for 90 days at 35°C in solutions containing monomethyl ethers based on ethylene glycol **Left to center** 2024-T351 aluminum. **Right to center** 7075-T651 aluminum. (**Front row**), extreme left and right: in distilled water. Other entries: under 50/50 by volume mixtures of distilled water with the compound noted. (**Back row**), extreme left and right: in salt solution. Other entries: under 50/50 by volume mixtures of salt solution with the compound noted. X axis – compound (see **Figure 1** for structures), Y axis - % weight gain. Compound 13, all Y ~ < 0.1 Wt.%.

The extent of oxidation developed in both aluminum alloys over a 90 day exposure to a 50/50 by volume mixture of these compounds with, either of, distilled water or salt solution,



was measured by gravimetry using methods outlined previously. Results are summarized in **Figure 9**. The weight gained by both alloys in distilled water and in salt solution (**Table 1**) are included for comparison. The weight gained by both aluminum alloys under 50/50 by volume mixtures of either EGME (11) or DIEGME (12) with either distilled water or salt solution was less than the weight gained under distilled water or salt solution alone. Both additives, therefore, appear to depress the oxidation of both alloys. Comparing results in distilled water, DIEGME appears to suppress oxidation of both alloys to a greater extent than EGME. However, the most interesting, and somewhat unexpected result, is the complete suppression of oxidation of both aluminum alloys under 50/50 by volume solutions of TRIEGME with either of distilled water or salt solution

## Conclusions

It has been observed that oxidation of both 2024-T351 and 7075-T651 aluminum model systems is suppressed under aqueous solutions containing longer chain, diol terminated oligomers of ethylene glycol. However, such oligomers are not soluble in kerosene based jet fuel to any useful level and, therefore, could not function as a reliable fuel system icing inhibitor (FSII) .

Diglyme, or compound 22, completely suppresses oxidation in 2024-T351 and 7075-T651 aluminum in aqueous solution and should be sufficiently miscible with JP-8 fuel to function as a FSII additive. However, it must be noted that the use of EGME, a prior FSII additive, was discontinued due to the toxicity of the compound. Diglyme is, if possible, more toxic than EGME. In addition, diglyme is an excellent paint stripper, and is somewhat more volatile than DIEGME, the current FSII additive in JP-8 fuel. As such, diglyme will be more

efficiently fractionated into low temperature distillates from the fuel than DIEGME. This could lead to more widespread instances of paint failure in B-52 integral wing fuel tanks.

Triethylene glycol monomethyl ether or TRIEGME has been evaluated previously as a FSII additive for kerosene based jet fuel<sup>(13)</sup>, and has been shown to perform better than DIEGME in that role. TRIEGME may, therefore, be effective at lower concentrations in the fuel. In addition, TRIEGME is less volatile than DIEGME and should be less efficiently fractionated into the vapor phase from JP-8 jet fuel. As such, the use of TRIEGME should lead to less paint failure in B-52 fuel tanks.

Finally, TRIEGME appears to passivate both 2024-T351 and 7075-T651 aluminum alloys towards oxidation in aqueous solution in the absence of microbial growth. As such, it would appear that TRIEGME should be given serious consideration as an alternate FSII additive in military jet fuel, and steps should be taken to elucidate mechanisms of passivation in the presence of this compound.

In subsequent work, the influence of EGME, DIEGME, and TRIEGME on paint delamination will be quantified as a function of FSII concentration in the fuel.

## Acknowledgements

The authors acknowledge financial support from the United States Air Force and the Boeing Military Company, without which this work would not have been possible. The authors acknowledge the technical support of Mr. Art. Porter, director of the CAD/CAM support facility at NIAR. The encouragement and support of Dr. John Tomblin, director of the National Institute for Aviation Research (NIAR) at Wichita State University is also acknowledged. **Figure 3** was constructed using data abstracted from reference 13.



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