

**A RAPID SURVEY OF THE COMPATIBILITY OF SELECTED SEAL MATERIALS
WITH CONVENTIONAL AND SEMI-SYNTHETIC JP-8**

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Synthetic JP-8**

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Opening remarks.

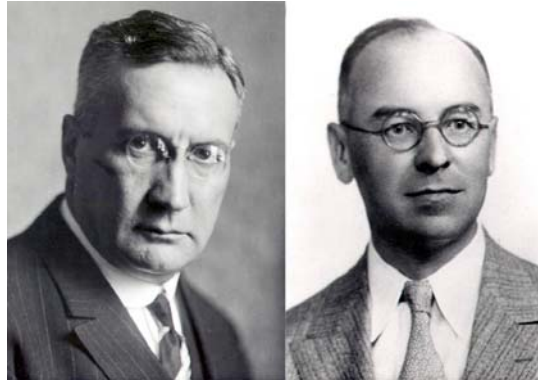
Since the synthesis of a liquid hydrocarbon fuel from coal by Franz Fischer and Hans Tropsch in 1923, there has been cyclic interest in developing this fuel for military and commercial applications. In recent years the U.S. Department of Defense has taken interest in producing a unified battlespace fuel using the Fischer Tropsch (FT) process for a variety of reasons including cost, quality, and logistics. In the past year there has been a particular emphasis on moving quickly to demonstrate that an FT fuel can be used in the form of a blend with conventional petroleum-derived jet fuel. The initial objective is to employ this semi-synthetic fuel with blend ratios as high as 50 percent FT with longer range goals to use even high blend ratios and ultimately a fully synthetic jet fuel. A significant concern associated with the use of a semi-synthetic jet fuel with high FT blend ratios is the effect these low aromatic fuels will have on fuel-wetted polymeric materials, most notably seals and sealants. These materials typically swell and soften to some degree when exposed to jet fuel and the aromatic content of these fuels contribute to this effect. Semi-synthetic jet fuels with very low aromatic contents may cause seals and sealants to shrink and harden leading to acute or chronic failure. Unfortunately, most of the material qualification tests are more concerned with excessive swelling than shrinkage and there is little guidance offered as to an acceptable level of shrinkage or other changes in physical properties related to low aromatic content. Given the pressing need for guidance data, a program was developed to rapidly survey the volume swell of selected fuel-wetted materials in a range of conventional and semi-synthetic jet fuels and through a statistical analysis to make a determination as to whether there was a basis to be concerned about using fuels with FT blend ratios as high as 50 percent. Concurrent with this analysis data was obtained as to the composition of the fuel absorbed in fuel-wetted materials through the use of GC-MS analysis of swollen samples as well as other supporting data. In this presentation the authors will present a summary of the results of the volume swell and fuel absorbed by selected O-rings and sealants as well as a description of the measurement protocols developed for this program.

Fischer-Tropsch Fuel

Developed by Franz Fischer and Hans Tropsch in 1923.

Hydrocarbon feedstocks are converted to carbon monoxide and hydrogen via high-temperature partial oxidation (Mond, 1879).

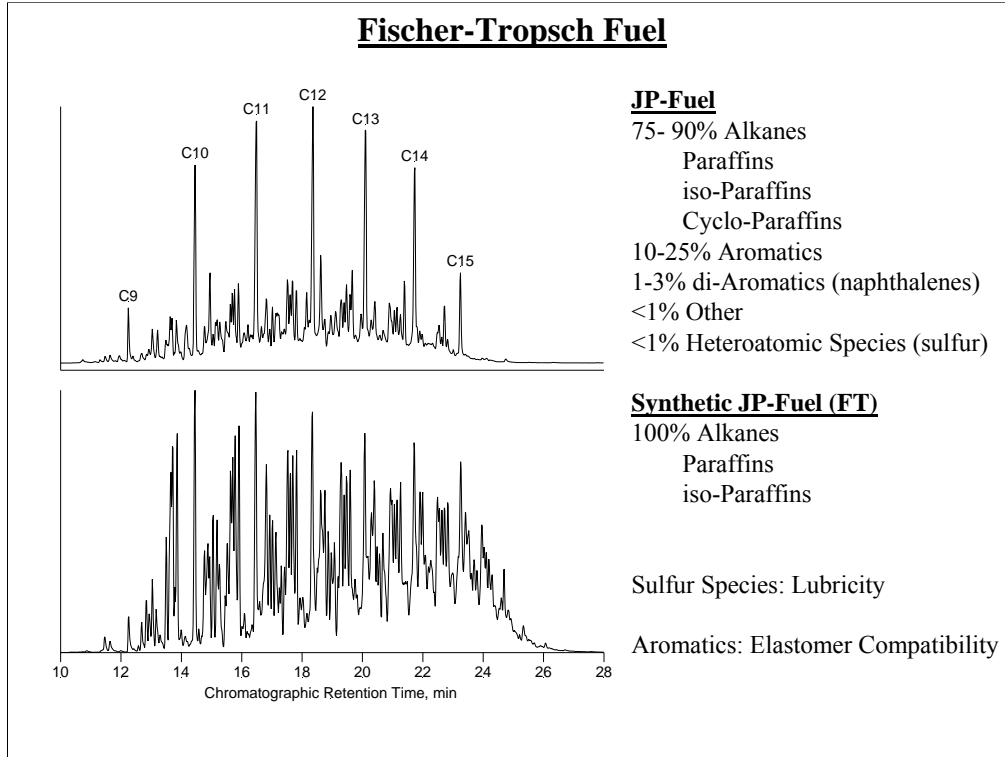
This mixture (called syngas) is then recombined over a catalyst to form a complex mixture of paraffins and iso-paraffins.



Franz Fischer

Hans Tropsch

When we talk about synthetic fuels we're almost always talking about the Fischer-Tropsch process.



In contrast FT fuel is composed entirely of paraffins and iso-paraffins....

Potential Strategies for Formulating FT Fuels

- 1) **Blend FT fuels with appropriate aromatics**
 - + Conceptually offers a relatively simple solution
 - 10-20% Aromatics will be required
 - Aromatics contribute undesirable characteristics
 - Which aromatics? Not all aromatics contribute equally to swell
- 2) **Blend FT fuels with something other than aromatics**
 - + Eliminates the problems associated with aromatics
 - + Could hopefully be added in very small amounts
 - + Offers opportunities for multi-functional additives
 - No swelling promoters are currently available for fuel
- 3) **Blend FT fuels with JP-8 (Semi-synthetic JP-8)**
 - + Potentially offers the simplest solution
 - + Presents the fewest unknowns to OEMs
 - + Operational experience with Sasol in South Africa
 - JP-8s are typically 75-90% paraffins (10-25% 'active' species)
 - By definition JP-8 behavior will be shifted towards FT
 - The range of acceptable blending ratios is uncertain

Common to all of these approaches is the issue of defining of an acceptable end-point

Potential strategies for making FT fuel compatible with conventional petroleum distillate fuels.

How do we define and acceptable end-point?

Qualification Tests for Material Physical Properties

Qualification tests for materials were written to qualify materials, not fuels.

Qualification tests were presumably written to qualify materials for service in petroleum distillate fuels such as JP-4 and JP-5.

Qualification tests often list maximum and/or minimum values following exposure in Type I and Type III reference fluids;

Type I	100% iso-Octane
Type III	30%v/v Toluene in iso-Octane

The maximum and minimum values specified in these tests does not necessarily mean that these are allowable in-service ranges, but rather these are initial values about which they are anticipated to vary by some nominal amount once in service.

For example, a common specification for O-rings is that they swell from 1-25% when aged in Type I and III fluids.

The existing material qualification tests do not provide adequate guidance to determine the compatibility of alternative fuels.

Specification tests for materials were written to qualify materials, not fuels.

Initial Flight Test Program: 25-50% FT/JP-8 Blend

Spring 2006

Plans were put in motion to perform a flight test with a semi-synthetic blend consisting of 25-50%v FT fuel in JP-8

Summer 2006

Ground tests at Tinker AFB

Fall 2006

Single-engine flight test (B-52) at Edwards AFB

Winter 2006

8-engine flight test (B-52) at Edwards AFB

Spring 2006

From a material compatibility perspective is safe to fly a 25-50%v FT fuel in JP-8?

Outline of an accelerated test plan in support of flight tests with semi-synthetic JP-8.

A Statistical Approach to Fuel Compatibility

The basis for a statistical approach to fuel compatibility is the fact that all materials presently in use have passed their respective qualification tests.

Through the course of normal use they are exposed to a range of JP-8s with a commensurate range of compositions, including aromatic content, and range of fuel/material interactions (e.g. volume swell).

If the behavior of an alternative fuel falls within the bounds of 'normal' JP-8 behavior, the fuel should be compatible with JP-8.

This approach does not necessarily demonstrate *absolute performance limits*, but rather provides guidance as to the degree of compatibility between JP-8 and an alternative fuel.

The basis for a statistical approach.

Experimental Program - Overall Approach

Obtain representative physical property data (volume swell) in a range of JP-8s to develop a statistical description of how a particular material behaves in 'normal' JP-8 ($\geq 10\%$ aromatics).

Obtain the same data in a semi-synthetic (FT/JP-8) fuel blend and compare these two populations to obtain a measure of the overlap between them.

Overall approach to employing a statistical model.

Experimental Program - Methods

Estimate the semi-volatile content of the original dry material

- + Thermogravimetric Analysis (TGA)
- + Provides an estimate of the propensity to shrink in fuel
- + Reconcile volume swell and fuel absorption data

Measure the amount and composition of the fuel absorbed

- + Direct Thermal Desorption GC-MS
- + Fuel/polymer partition coefficients
- + Estimate the relative contributions of aromatics and alkanes

Measure the volume swell

- + Optical Dilatometry
- + Relatively simple *in situ* method based on digital imaging
- + Provides temporal information

All of these methods use small samples (1-5 mg samples in 1-10 mL of fuel) and are suitable for high-throughput testing.

Experimental methods.

Test Matrix

10 Neat Fuels (9 JP-8s and 1 FT fuel)
30 Blends (25%, 37.5%, 50%, and 75%v/v FT)

29 Non-metallic Materials

6 Sealants	2 Bladders
4 O-rings	2 Hoses
4 Films	2 Composites
3 Coatings	1 Foam
3 Adhesives	3 Miscellaneous

O-rings

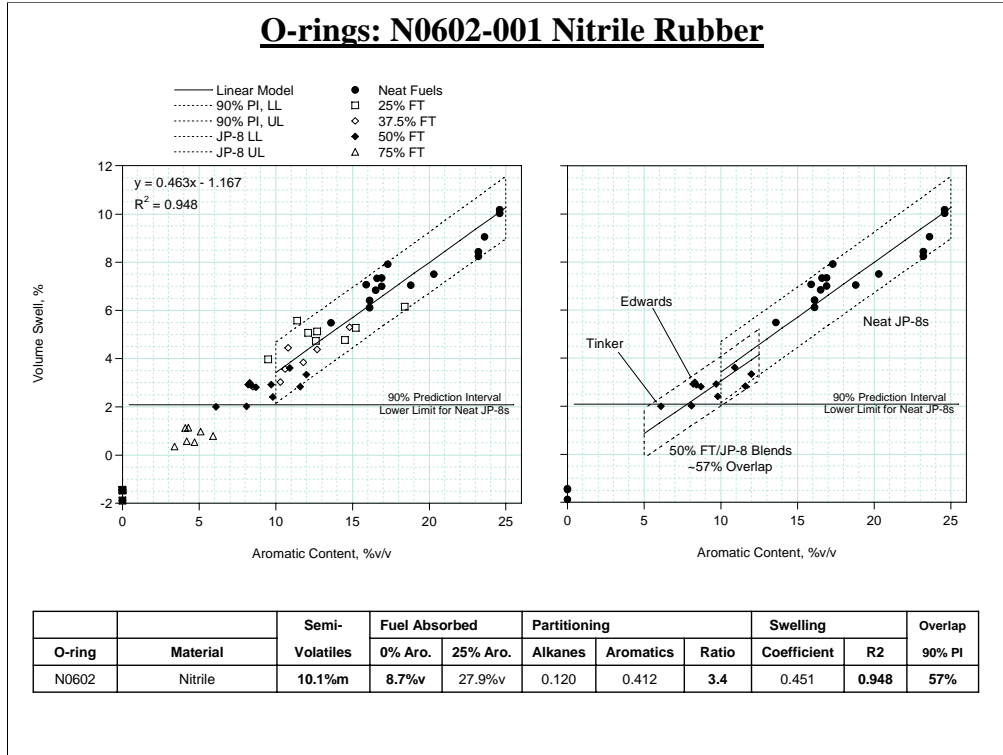
Nitrile Rubber
Fluorosilicone
Fluorocarbon (2)

Sealants

Polythioether/Polyurethane
Fluorosilicone
Polysulfide (3)
Polythioether

Test Matrix

O-rings: N0602-001 Nitrile Rubber



Results summary.

Semi-volatile content (TGA) reflects the propensity of a material to shrink.

Comparing the fuel absorbed with the semi-volatiles lost is an indicator of the balance between material to the fuel and gained from the fuel.

Partitioning reflects the sensitivity to the aromatic content.

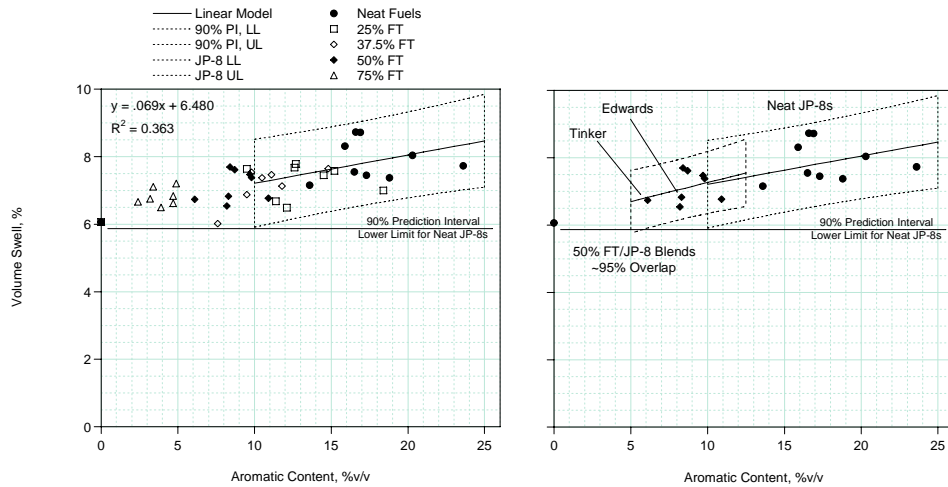
The swelling coefficient reflects the overall result of the polymer:fuel interaction.

The coefficient of determination (R2) reflects the strength of the correlation between the volume swell and aromatic content of all JP-8s.

The overlap between the 90% prediction intervals for the 50% fuel blends and the parent fuels is an approximate measure of the degree of compatibility between the test material and 'normal' JP-8s.

Note that in many cases the distribution narrows as the concentration of aromatics approaches zero.

O-rings: L1120-001 Fluorosilicone



O-ring	Material	Semi-Volatiles	Fuel Absorbed		Partitioning			Swelling		Overlap 90% PI
			0% Aro.	25% Aro.	Alkanes	Aromatics	Ratio	Coefficient	R2	
L1120	Fluorosilicone	0.0% <i>m</i>	5.0% <i>v</i>	7.9% <i>v</i>	0.057	0.105	1.8	0.069	0.363	95%

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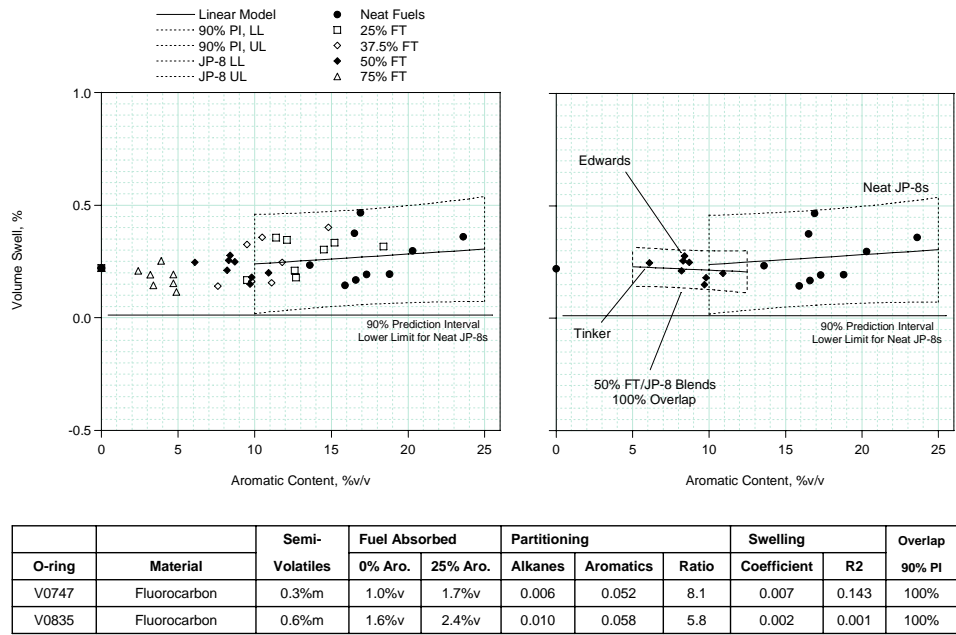
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O-rings: V0747 & V0835 Fluorocarbon



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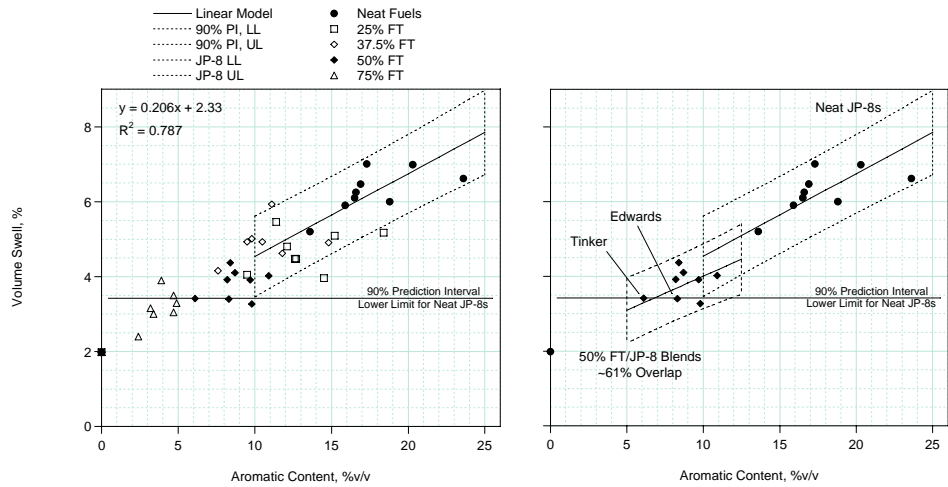
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Sealants: PR-2911 Polythioether/Polyurethane



Sealant	Material	Semi-Volatiles	Fuel Absorbed		Partitioning			Swelling		Overlap 90% PI
			0% Aro.	25% Aro.	Alkanes	Aromatics	Ratio	Coefficient	R2	
PR-2911	Polythioether/Polyurethane	0.0% _m	5.5% _v	13.4% _v	0.059	0.231	3.9	0.206	0.787	61%

Results summary.

Semi-volatile content (TGA) reflects the propensity of a material to shrink.

Comparing the fuel absorbed with the semi-volatiles lost is an indicator of the balance between material to the fuel and gained from the fuel.

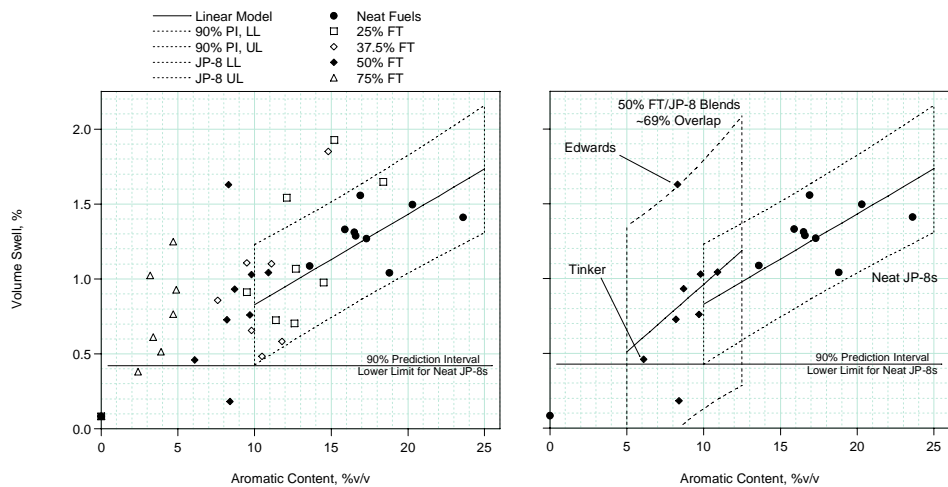
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Sealants: Q4-2817 Fluorosilicone

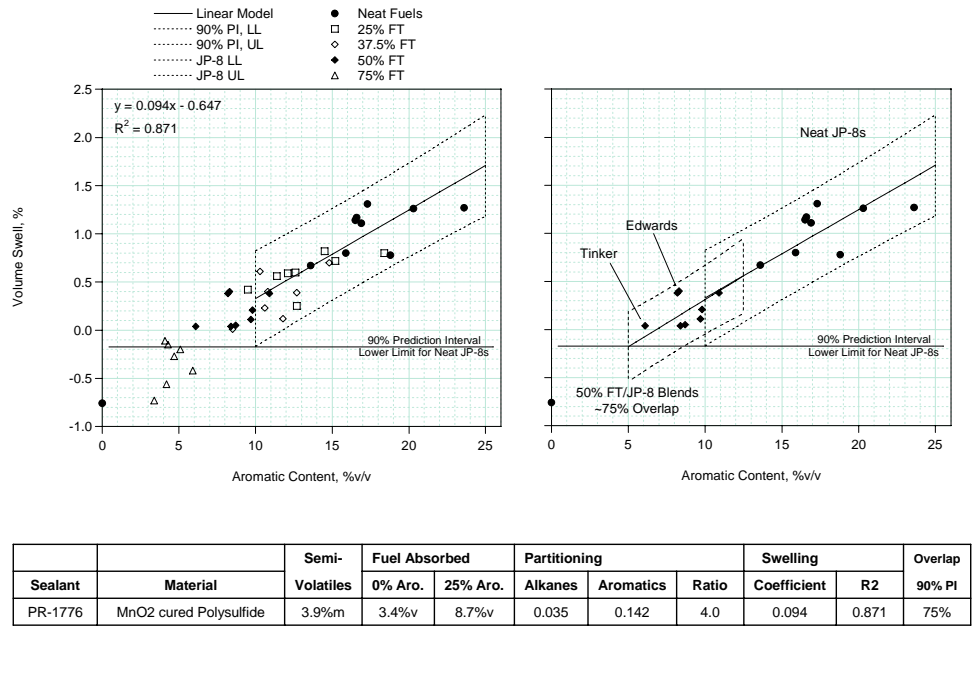


Sealant	Material	Semi-Volatiles	Fuel Absorbed		Partitioning			Swelling		Overlap 90% PI
			0% Aro.	25% Aro.	Alkanes	Aromatics	Ratio	Coefficient	R2	
Q4-2817	Fluorosilicone	4.3% _m	2.9% _v	3.0% _v	0.026	0.080	3.1	0.052	0.419	69%

Results summary.

- Semi-volatile content (TGA) reflects the propensity of a material to shrink.
- Comparing the fuel absorbed with the semi-volatiles lost is an indicator of the balance between material to the fuel and gained from the fuel.
- Partitioning reflects the sensitivity to the aromatic content.
- The swelling coefficient reflects the overall result of the polymer:fuel interaction.
- The coefficient of determination (R2) reflects the strength of the correlation between the volume swell and aromatic content of all JP-8s.
- The overlap between the 90% prediction intervals for the 50% fuel blends and the parent fuels is an approximate measure of the degree of compatibility between the test material and 'normal' JP-8s.

Sealants: PR-1776 MnO₂ Cured Polysulfide



Results summary.

Semi-volatile content (TGA) reflects the propensity of a material to shrink.

Comparing the fuel absorbed with the semi-volatiles lost is an indicator of the balance between material to the fuel and gained from the fuel.

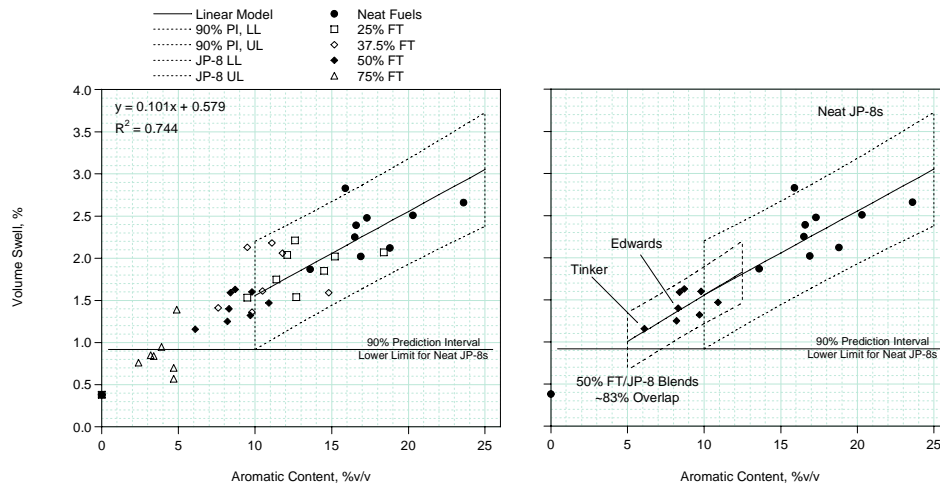
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Sealants: PR-1422 Cr₂O₇ Cured Polysulfide



Sealant	Material	Semi-Volatiles	Fuel Absorbed		Partitioning			Swelling		Overlap 90% PI
			0% Aro.	25% Aro.	Alkanes	Aromatics	Ratio	Coefficient	R2	
PR-1422	Cr2O7 cured Polysulfide	1.9% _m	2.8% _v	9.9% _v	0.033	0.164	4.9	0.101	0.744	83%

Results summary.

Semi-volatile content (TGA) reflects the propensity of a material to shrink.

Comparing the fuel absorbed with the semi-volatiles lost is an indicator of the balance between material to the fuel and gained from the fuel.

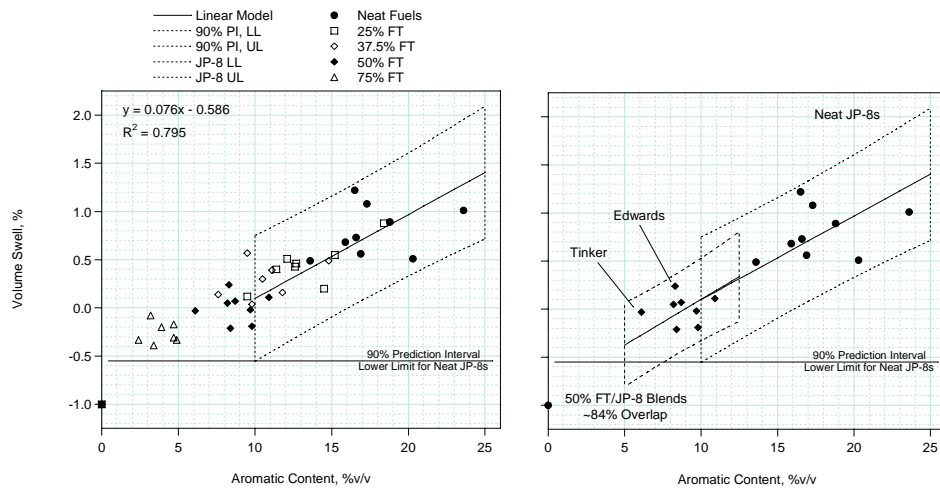
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The swelling coefficient reflects the overall result of the polymer:fuel interaction.

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The overlap between the 90% prediction intervals for the 50% fuel blends and the parent fuels is an approximate measure of the degree of compatibility between the test material and 'normal' JP-8s.

Sealants: PR-1440 MnO₂ Cured Polysulfide



Sealant	Material	Semi-Volatiles	Fuel Absorbed		Partitioning			Swelling		Overlap 90% PI
			0% Aro.	25% Aro.	Alkanes	Aromatics	Ratio	Coefficient	R2	
PR-1440	MnO ₂ cured Polysulfide	3.0% _m	2.9% _v	7.1% _v	0.021	0.137	6.5	0.076	0.795	84%

Results summary.

Semi-volatile content (TGA) reflects the propensity of a material to shrink.

Comparing the fuel absorbed with the semi-volatiles lost is an indicator of the balance between material to the fuel and gained from the fuel.

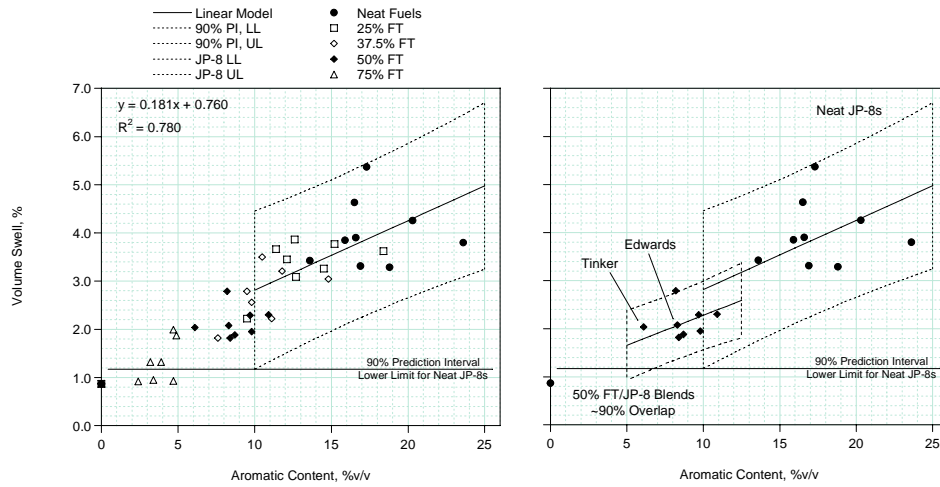
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The overlap between the 90% prediction intervals for the 50% fuel blends and the parent fuels is an approximate measure of the degree of compatibility between the test material and 'normal' JP-8s.

Sealants: PR-1828 Epoxy Cured Polythioether



Sealant	Material	Semi-Volatiles	Fuel Absorbed		Partitioning			Swelling		Overlap 90% PI
			0% Aro.	25% Aro.	Alkanes	Aromatics	Ratio	Coefficient	R2	
PR-1828	Epoxy cured Polythioether	2.3%	2.0%	9.5%	0.025	0.172	7.0	0.181	0.780	90%

Results summary.

Semi-volatile content (TGA) reflects the propensity of a material to shrink.

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Summary

O-rings

O-ring	Material	Semi-	Fuel Absorbed		Partitioning			Swelling		Overlap 90% PI
		Volatiles	0% Aro.	25% Aro.	Alkanes	Aromatics	Ratio	Coefficient	R2	
N0602	Nitrile	10.1% _m	8.7% _v	27.9% _v	0.120	0.412	3.4	0.451	0.948	57%
L1120	Fluorosilicone	0.0% _m	5.0% _v	7.9% _v	0.057	0.105	1.8	0.069	0.363	95%
V0747	Fluorocarbon	0.3% _m	1.0% _v	1.7% _v	0.006	0.052	8.1	0.007	0.143	100%
V0835	Fluorocarbon	0.6% _m	1.6% _v	2.4% _v	0.010	0.058	5.8	0.002	0.001	100%

Sealants

Sealant	Material	Semi-	Fuel Absorbed		Partitioning			Swelling		Overlap 90% PI
		Volatiles	0% Aro.	25% Aro.	Alkanes	Aromatics	Ratio	Coefficient	R2	
PR-2911	Polythioether/Polyurethane	0.0% _m	5.5% _v	13.4% _v	0.059	0.231	3.9	0.206	0.787	61%
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PR-1776	MnO2 cured Polysulfide	3.9% _m	3.4% _v	8.7% _v	0.035	0.142	4.0	0.094	0.871	75%
PR-1422	Cr2O7 cured Polysulfide	1.9% _m	2.8% _v	9.9% _v	0.033	0.164	4.9	0.101	0.744	83%
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Results summary.

Conclusions

We have developed a statistical approach to estimate the material compatibility of synthetic and semi-synthetic fuels with JP-8.

The method is based on comparing a characteristic response (volume swell) of a material in a reference population of 'normal' JP-8s and in the test fuel.

To-date we have completed the analysis of selected O-rings, sealants, fuel barrier materials, adhesives and composites.

To-date, none of these materials have indicated there will be an acute problem operating with 50% FT fuel blends.

The materials that are of greatest concern are the nitrile and nitrile-like materials, especially those with high plasticizer contents.

Some caution needs to be exercised in interpreting the results for materials that rely on physical properties that may not be reflected in the volume swell, most notably interfacial adhesion (adhesives, composites, sealants).

Conclusions.

Future Work

Complete the present test program including obtaining data on the remaining samples.

Extend the program to include other fundamental physical properties such as compressive modulus and adhesion.

The database of JP-8s should be expanded to establish a more complete statistical description of the population of JP-8s.

Suitable methods and reference materials should be developed to circumvent the problem of variations in test materials. This may be accomplished through the use of parallel analysis of samples in selected reference fluids.

Apply this approach to the development of a fully synthetic JP-8. For example, a JP-8 with selected additives and/or a non-petroleum source of aromatics.

Future work.

Acknowledgements

We would like to gratefully acknowledge the United States Air Force, AFRL/PRTG and the United States Department of Energy for supporting this work.

I'd also like to acknowledge the tireless work of Doug Wolf and his co-workers in the UDRI Micro Analytical Laboratory for their work on the optical dilatometry.

And finally, I'd like to acknowledge my students; Chad Huelsman, Valerie Sutton, and George Fels for their hard work.

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Questions?