Biodiesel:

Compatibility and Regulation

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Today's topics:

 10 ways biodiesel blends may adversely effect material compatibility

... and how to avoid 9 of those.

 B100: why California has declared it a "hazardous substance"





10 ways **BIODIESEL** may reduce material stability in UST systems

- Is more electrically conductive than diesel > corrosive
- 2. Oxidation produces corrosive conditions
- Has often been out-of-spec in the past > can create corrosive conditions
- 4. Is a solvent that may degrade some elastomers
- Exhibits adverse effects on some elastomers only after 300 hours of testing –





10 ways **BIODIESEL** may reduce material stability in UST systems

- 6. Effects may depend on elastomer curing methods
- 7. Is more aggressive when water contaminated
- 8. Is more aggressive in acidic conditions
- 9. Is more aggressive with age
- 10. With new technology, 'it's always something'.





#1 Biodiesel is more electrically conductive than petroleum diesel

greater potential for corrosion

for example





Conductivity of Various Biodiesel Blends vs. #2 Fuel Oil (pS/m)

#2 Fuel Oil	Biodiesel %	Biodiesel %	Biodiesel %	Biodiesel %	Biodiesel %
0 %	2 %	20 %	40 %	60 %	100 %
2	7	75	358	775	1209

Courtesy of the National Biodiesel Board. Testing conducted by Williams Pipeline.





The greater electrical conductivity can cause galvanic metal corrosion in vulnerable metals

Copper, bronze, brass, aluminum, lead, tin, zinc...

... but biodiesel may cause significant metal corrosion in other ways

even in steel UST





2 Biodiesel oxidation produces corrosive peroxides

Example: 10' diameter steel UST walls are ~ 6mm 0.2 % H2O2 corrosion rate on 1030 steel ~ 2mm/yr

Are the peroxides produced in biodiesel oxidation capable of penetrating a steel UST in 3 years?

Not impossible if the UST is routinely exposed to contaminated fuel, water, and acidity





#3 Biodiesel has frequently been out of spec in the past

In 2007 National Renewable Energy Lab published a nationwide survey of B100 fuel quality

- >50% B100 samples did NOT meet ASTM D6751
- Off spec fuel may contain corrosive contaminants such as peroxides and water





#4 Biodiesel is a solvent that may attack some elastomers under specific conditions

Volume change may exceed 100%

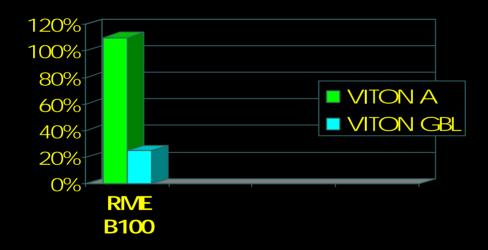
 Hardness and tensile strength may decrease more than 50%





Biodiesel [B100]: Elastomer Swelling in Viton®

note: these elastomers are stable in petroleum-based CARB gasoline and ULSD



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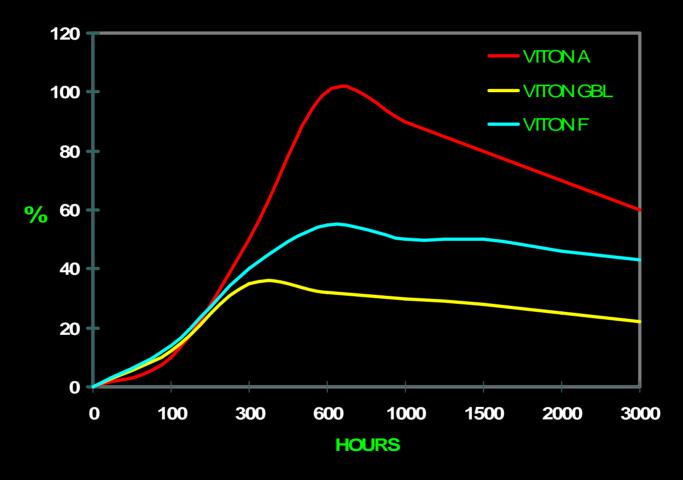
#5 Changes in elastomer properties due to biodiesel may be delayed

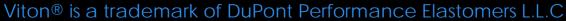
- One might expect most significant physical property changes to occur within 100 hours of fuel exposure, but
- new data indicate very significant changes occur only after 300 to 1000 hours





Biodiesel [B100]: Volume Change over 3000 hours









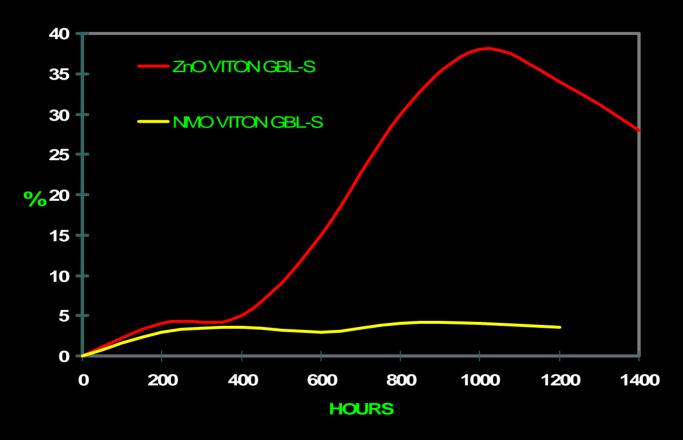
#6 Biodiesel may degrade elastomers that are cured using metal oxides.

- ... for example, VITON® GBL-S cured with metal oxides swells nearly 10X greater
- ... than the same VITON® GBL-S cured without metal oxides.
- Metal oxides are routine ingredients in all fluoroelastomer formulations and needed for bisphenol cured fluoroelastomers such as VITON® A401C.
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B20: meets ASTM D6751 Total Acid Number Swelling w/wo Zinc Oxide Curing







#7 Water contamination makes biodiesel more aggressive

- Water facilitates electrical conductivity
- Water accelerates oxidation
- Water often contains other contaminants such as salts
- maintain dry tanks and insist on dry fuel





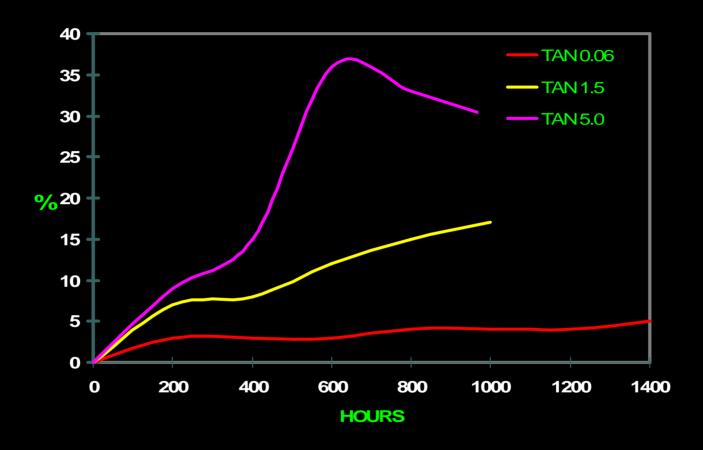
#8 Acidic conditions make biodiesel more aggressive to some polymers

- ASTM 6751-07a TAN spec is 0.5 max (mgKOH /kg)
- Acids may be byproduct of biodiesel oxidation
- ... acidic conditions exceeding this spec can increase swelling
 - ... for example, the volume increase effect of
- B20 at 3 acid levels on
- VITON® A401C over 1000 hours:





B20: Effect of Acidity on Swelling in VITON A®



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#9 Aging makes biodiesel more aggressive

- "old" biodiesel causes greater damage to elastomers than "new" biodiesel
- "Old" = 6-8 weeks since production
- Tensile strength decreases 70%-80%
- Volume increases more than 100%

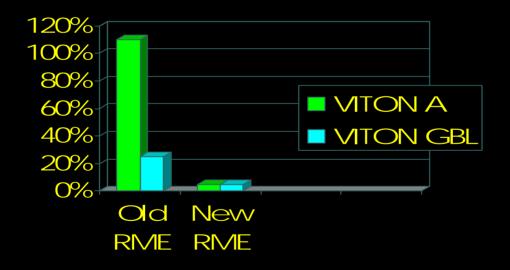
... for example,





Biodiesel [B100]: Effects on Swelling; Old vs. New

note: these elastomers are stable in petroleum-based CARB gasoline and ULSD

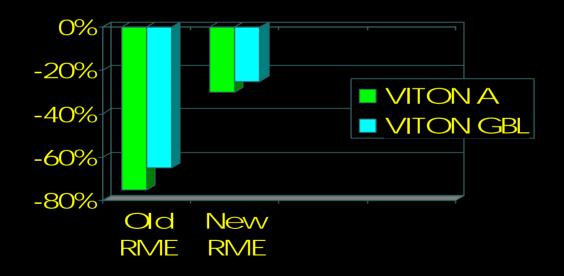






Biodiesel [B100]: Tensile Strength Loss; Old vs. New

note: these elastomers are stable in petroleum-based CARB gasoline and ULSD







How do you choose elastomers for storing biodiesel?

Consult polymer manufacturers for recommendations on the most cost effective elastomer and grade for the fuel blend stored.





Why is elastomer "GRADE" important?

- VITON ® fluoroelastomers are widely used in UST systems storing biodiesel
- ... and are available in many grades: A, B, F, GB, GBL, GF, GFLT, etc.
- VITON A is NOT recommended for storing biodiesel,
- ... however, other VITON grades are very stable when exposed to biodiesel blends.

• Viton® is a trademark of DuPont Performance Elastomers L.L.C.





Why the California State Water Board considers B100 a hazardous substance

- California statutes have NO de minimus limitations
- ASTM D6751-07a allows up to 0.5% Methanol,
 --- which is a "hazardous" substance
- Out of spec biodiesel may contain "hazardous" peroxides ...

unless antioxidants have been added

... however, antioxidants are themselves usually <u>"hazardous" substances</u>





10 ways **BIODIESEL** may reduce material stability in UST systems –

and what to do about it

Biodiesel:

- Is more electrically conductive; avoid vulnerable metals and water
- Is vulnerable to oxidation: avoid off-spec fuel, water, and "old" fuel (biodiesel not recommended for standby generators)
- Has been frequently contaminated: insist on guarantee of ASTM D6751 fuel quality





10 ways **BIODIESEL** may reduce material stability in UST systems –

and what to do about it

Biodiesel

- #4 Is a solvent that attacks elastomers: ask polymer manufacturers for advice
- #5 Effects may be slow to appear: select UST system components tested at > 500 hours exposure.
- #6 Attacks elastomers based on curing method: ask polymer manufacturers for advice
- #7 Is more aggressive in the presence of water: Duh, avoid water in UST and fuel.





10 ways **BIODIESEL** may reduce material stability in UST systems –

and what to do about it

Biodiesel:

#8. Is more aggressive in acidic conditions: avoid off-spec fuel, water, and vulnerable metals

#9. Is more aggressive as it ages: supplier should provide "Rancimat" test certification on each fuel drop,

#10 With new technology, it's always something ...





#10 With new technology, it's always something ...



If there's a 50-50 chance of something else going wrong,...

there's a 90% chance it will. Yogi Berra?





CONCLUSIONS about BIODIESEL:

- Water, acidity, curing method, & grade are all factors in elastomer stability
- Some elastomers may not show signs of degradation for >400 hours
- 3. Contaminated fuel, peroxides, & conductivity all contribute to potential for metal corrosion





RECOMMENDATIONS for storing BIODIESEL:

- Consult elastomer manufacturers re most cost effective options
- Avoid and replace vulnerable metals!!
- 3. Insist on fuel quality guarantees!!!
- 4. Keep the UST and fuel water-free!!!





Trust data, not intuition

5. The effects of biodiesel on UST material stability are NOT intuitive ...

DuPont findings are case in point

compatibility testing = assume worst-case, real-world conditions, w/extended tests





Biodiesel:

Terminology, Compatibility, Regulation

Thank you for your attention

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Archive of old slides

Stable Materials for Storing Biodiesel

A partial list

Teflon (polytetrafluoroethylene PTFE)

Tefzel and Fluon (ethylene-tetrafluoroethylene, ETFE)

Viton (only grades GB, GBL, GF, GFL -- all are fluoroelastomers, FKM)

Kalrez (Spectrum 6375, Spectrum 7075, and 4079), Technoflor FFKM, Zalak 250GP, and Zlx (perfluoroelastomers, FFKM)

Chemraz (not DuPont)

Vamac; ethylene acrylic elastomer G, GLS, GXF or HVG terpolymers





Materials to Avoid when Storing BIODIESEL

A partial list

Polycholoroprene

Nitrile, Hydrogenated HNBR

Butadiene BR

Hypalon CSM (chlorosulfonated polyethylene)

Natural Rubber NR (Isoprene)

Neoprene

Polystyrene

Styrene-Butadiene SBR

Polyethylene

Polysulfide

Ethylene Propylene EPDM

Nitrile NBR #





OK, elastomer grade is important,

... but are the stable VITON grades the only elastomers compatible with biodiesel?

no... other fluoropolymers are also compatible for example...





fluoropolymers are very stable, but there are cost-benefit tradeoffs

In descending order of stability and price:

- Fluoroelastomers (FKM) "VITON ®"
- Polytetrafluoroethylene (PTFE) "Teflon ®"
- Perfluoroelastomers (FFKM) "KALREZ ®"
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 L.L.C.; Teflon® is a trademark of DuPont





OK, ... fluoroelastomers, but which one?

- Kalrez and Teflon are more stable than the stable grades of VITON,
 - but they are also much more expensive
- so consult polymer manufacturers for the most cost effective choice of polymer grade for the fuel stored!
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 Teflon® is a trademark of DuPont





Biofuels Terminology

Despite confusing media reports to the contrary...

"Biodiesel" and "Renewable Diesel" are two different fuels via different processes

True, both are "renewable" and both can be made from animal fats

... but despite being renewable and despite using the same feedstocks, the final fuels are NOT chemically similar





Biofuels Terminology

- The transesterification process converts animal fat into a renewable methyl ester fuel defined as "Biodiesel"
- Conoco-Phillips reports they have developed a process* that also converts animal fat into a renewable diesel fuel called "Renewable Diesel"...
- ... by depolymerizing animal fat triglycerides into three diesel molecules and one propane molecule either by decarboxilation or hydrogenation.
- The diesel fuel produced is a linear paraffin, an alkane, that resembles low-temperature Fischer Tropsch products.





Biofuels Terminology

This is important because ...

One might assume the effects of **methyl ester** fuels and **alkanes** fuels on UST systems are **NOT** the same ...

But there is not sufficient data on **alkane** fuels to make any comparison.

Consequently, this presentation is only about biodiesel (methyl ester) effects on UST systems



