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# Corrosion issues of ethanol blends and the effect of water

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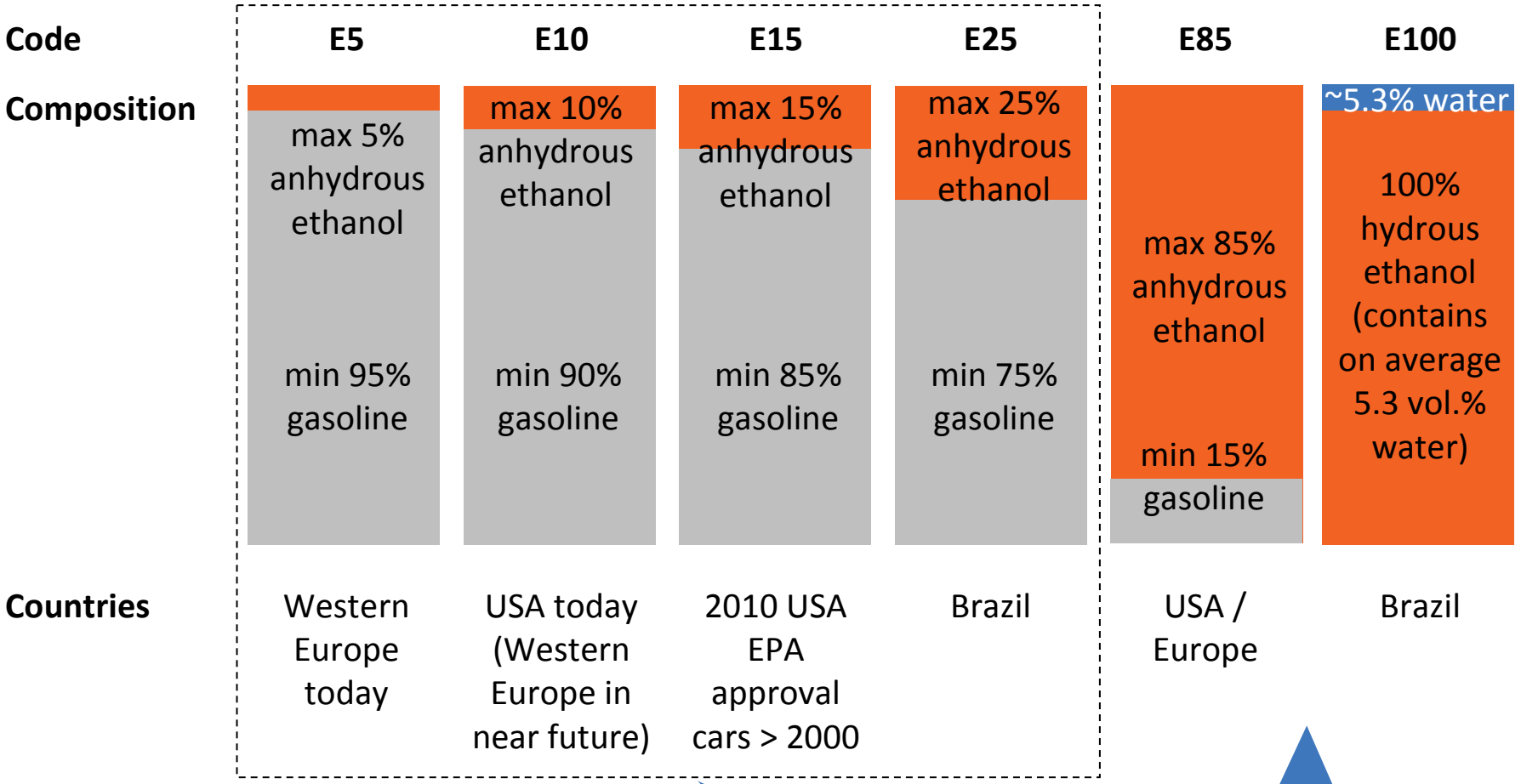
# Composition of ethanol containing fuels



# Two basic types of corrosion

- **Electrochemical corrosion "wet corrosion"**

  Facilitated by conductivity especially in case of phase separation and the formation of a water layer in low blends (<E10)

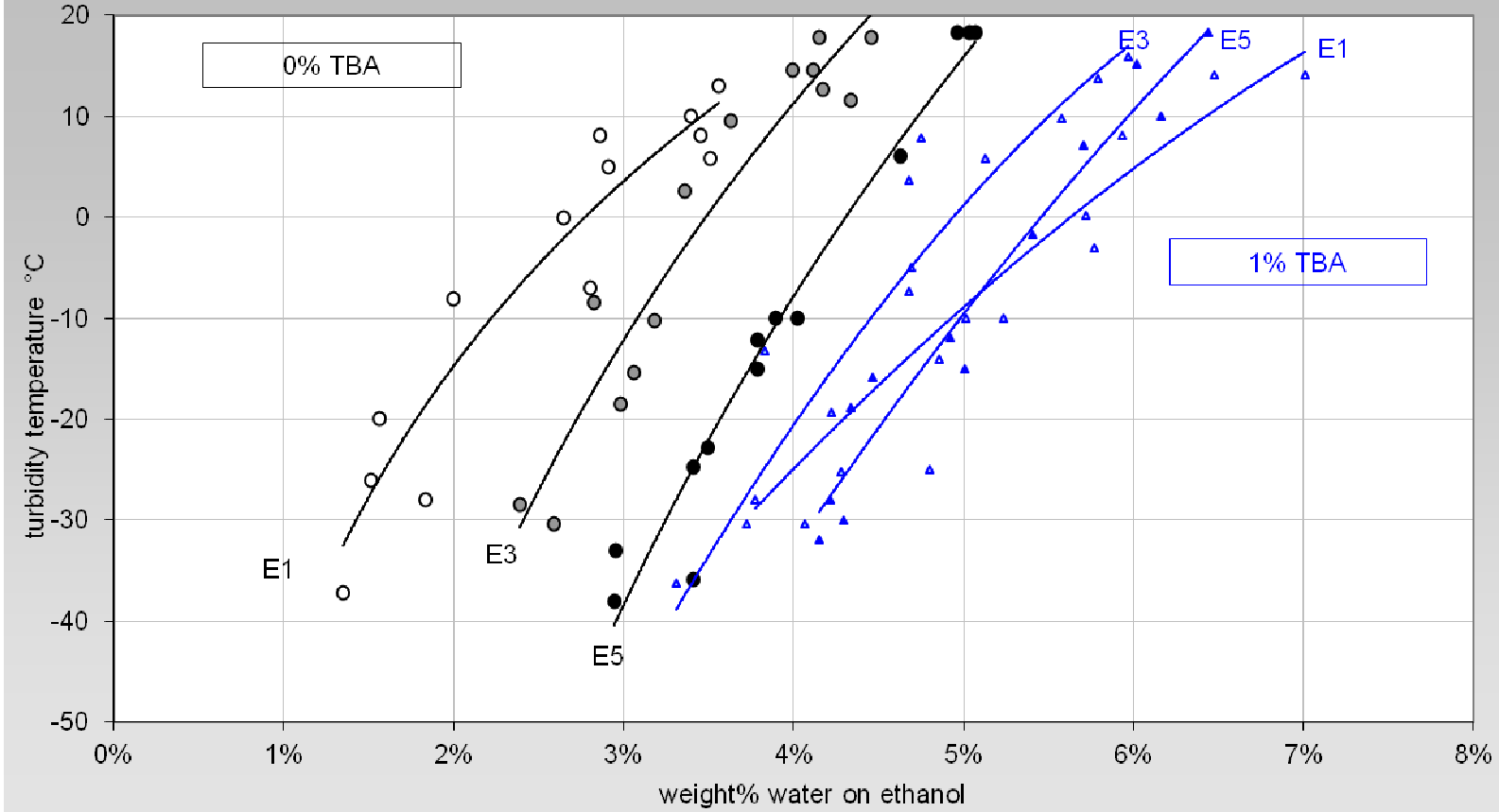
Corrosion at the bottom of a tank after phase separation of water
*Source: METI, Japan*

- **Alcoholate (alkoxide) corrosion "dry corrosion"**

"dry" alcoholate corrosion of a cast Al-alloy in an E10 gasoline blend

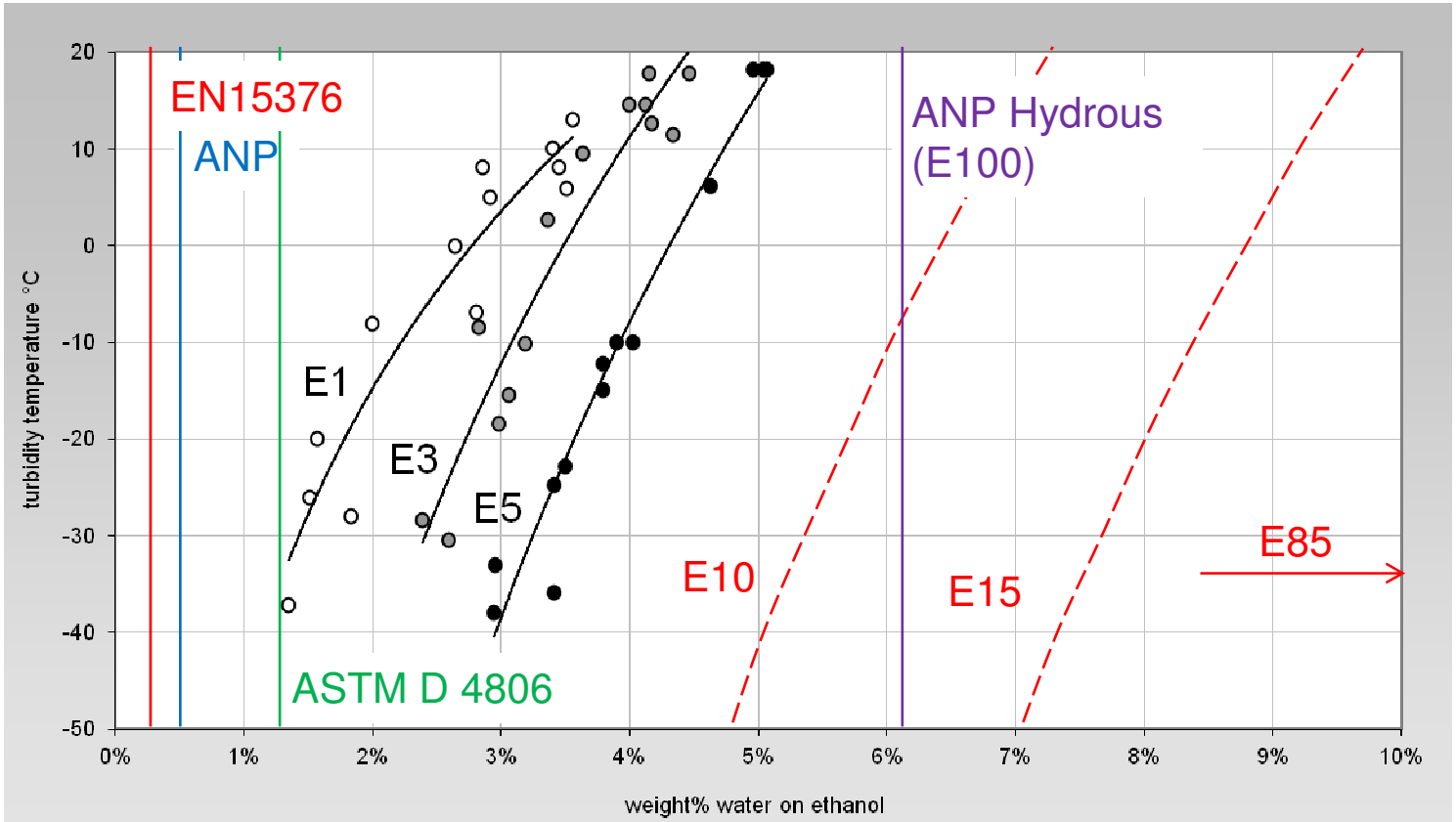
*Source:* TECHNISCHE UNIVERSITÄT DARMSTADT; MPA Darmstadt IfW; Fraunhofer LBF; SzM

# CONCAWE – 2008 Ethanol Report
# Phase Stability Ethanol Blends




Terschel, DGMK (German Society for Petroleum and Coal Science and Technology) report 645 (2005)

# Phase Stability Ethanol Blends Continued




Data points: Terschel, DGMK (German Society for Petroleum and Coal Science and Technology) report 645 (2005)

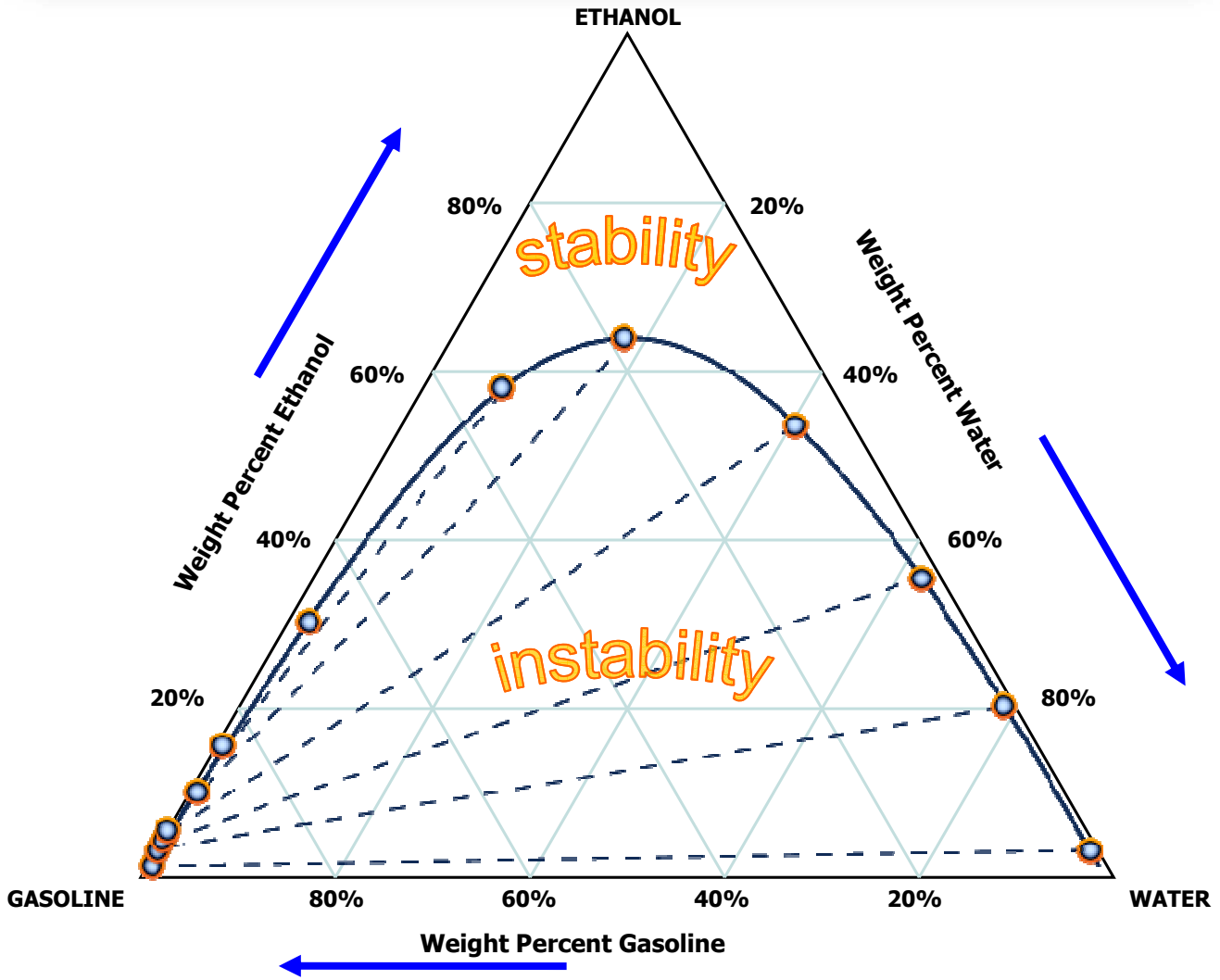
# Wet Corrosion Tests by Sasol

- **Sasol's "wet corrosion" tests (ASTM D665) of E2 and E10 on aluminum parts.**
  - Wet corrosion is corrosion in the presence of water

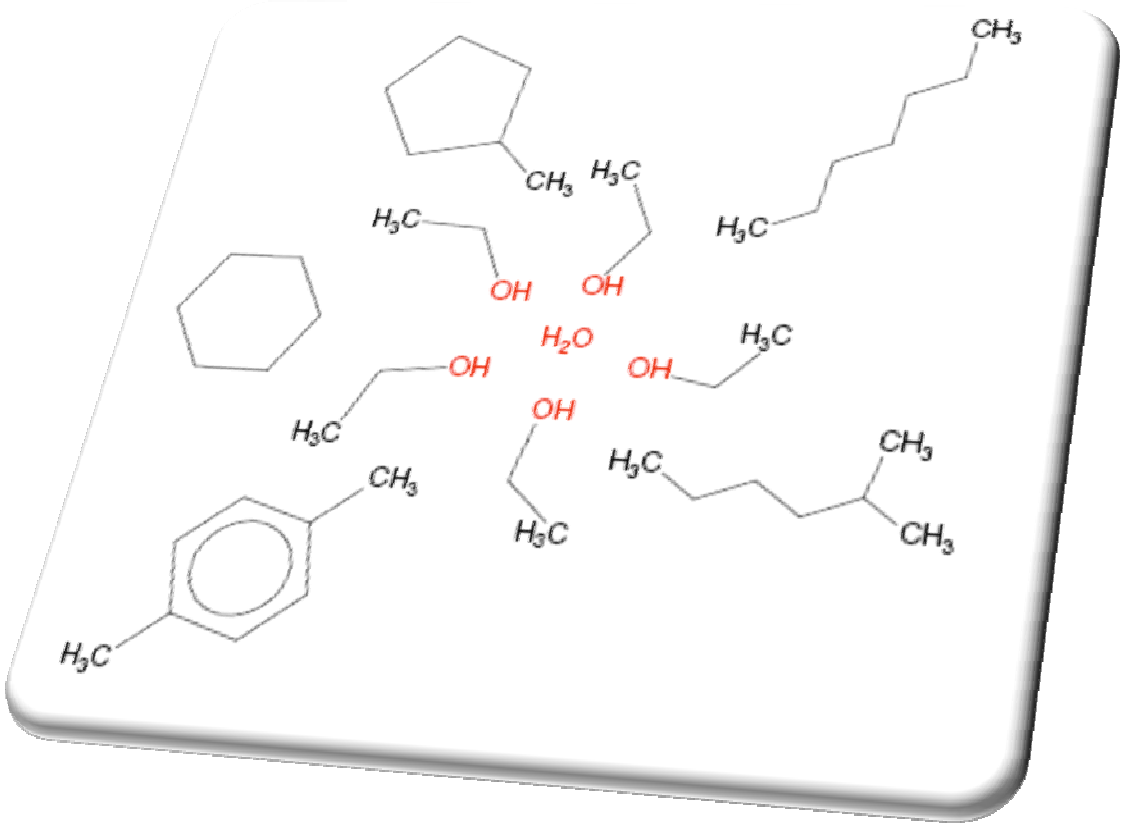
- **Sasol found:**
  - Both the base gasolines as well as the ethanol containing fuels (at 2% ethanol content) were corrosive during the wet corrosion test.
  - These fuels required additisation in order to prevent wet corrosion.
  - At 10% ethanol (bioethanol and synthetic ethanol) none of the fuels were corrosive in the wet corrosion test.

*Presented at the XVIII International Symposium on Alcohol Fuels*
*(Delhi – India ISAF 2010)*

# Wet Corrosion & Phase Separation



# Capture H2O



# Conductivity E10's adding salt water

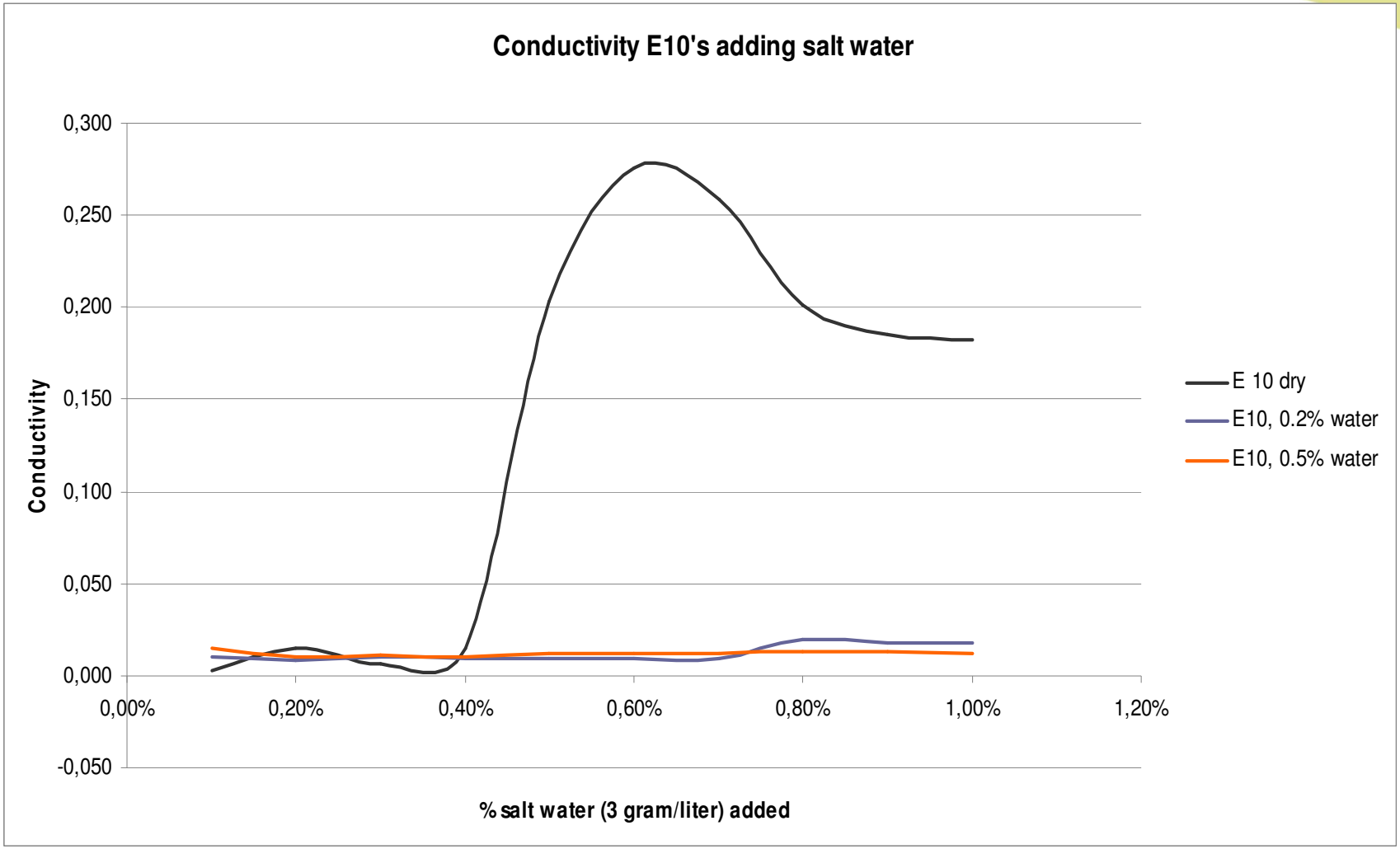
| Salt Water | E10, dry | E10, 0.2% water | E10, 0.5% water |
|---|---|---|---|
| 0,10% | 0,003 | 0,010 | 0,015 |
| 0,20% | 0,015 | 0,008 | 0,010 |
| 0,30% | 0,006 | 0,010 | 0,011 |
| 0,40% | 0,015 | 0,009 | 0,010 |
| 0,50% | 0,203 | 0,009 | 0,012 |
| 0,60% | 0,276 | 0,009 | 0,012 |
| 0,70% | 0,259 | 0,009 | 0,012 |
| 0,80% | 0,201 | 0,020 | 0,013 |
| 0,90% | 0,185 | 0,018 | 0,013 |
| 1,00% | 0,182 | 0,018 | 0,012 |

Test by SGS last week to see if more hydrous E10 picks up more salts?

salt drops out

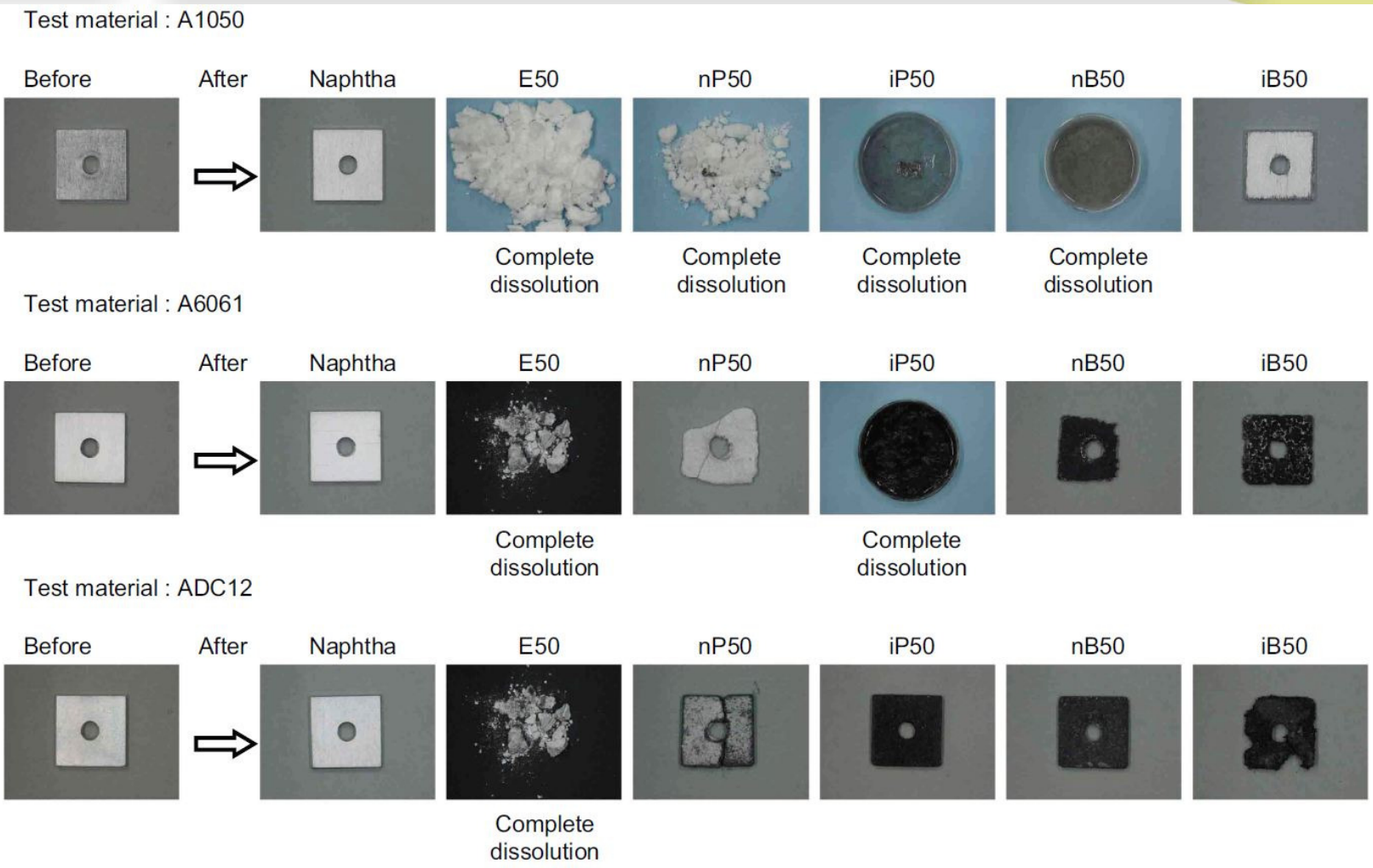
free water

# Conductivity E10's adding salt water



# Dry Corrosion Research Japan (JARI)






Appendix 3.1 Photographs of the immersion test results using a single alcohol fuel.
(Alcohol content : 50%, Water content : 150ppm).

# Dry Corrosion Research Japan (JARI)



| Material in fuel system | Type | Gasoline 100% | E50 with 150 ppm water (overall) * | E50 with 500 ppm water (overall) * | E50 with 2000 ppm water (overall) * | E50 with 10.000 ppm water (1%, overall) * |
|---|---|---|---|---|---|---|
| Aluminum | A1050 | OK | complete dissolution | complete dissolution | complete dissolution | OK |
| Aluminum | A6061 | OK | complete dissolution | complete dissolution | OK | OK |
| Aluminum | ADC12 | OK | reduction in mass | reduction in mass | OK | OK |
| Steel | | change in surface | OK | OK | OK | change in surface |
| Copper | | change in surface | change in surface | change in surface | change in surface | change in surface |
| Nickel | | OK | OK | OK | OK | OK |
| Zinc | | OK | change in surface | change in surface | OK | change in surface |
| Tin | | OK | change in surface | change in surface | change in surface | OK |

**Legend:**

| | |
|---|---|
| OK | *No change observed* |
| change in surface | *change in color for instance, but no reduction in mass* |

* *1 vol% overall water in E50 means a concentration of 2 vol% water in the added ethanol*

## Alcoholate corrosion of aluminum

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- Refers to the chemical corrosion of metals in the presence of fuel alcohol containing fuel blends
- Alcohols can react with aluminium alloys, lead and magnesium with the formation of alkoxide or alcoholate corrosion products

$$3C_2H_5OH + Al \rightarrow (C_2H_5O)_3Al + 3/2H_2 \quad (1)$$

$$(C_2H_5O)_3Al + 3H_2O \rightarrow Al(OH)_3 + 3C_2H_5OH \quad (2)$$

$$(C_2H_5O)_3Al \rightarrow Al_2O_3 + 6C_2H_4 + 3H_2O \quad (3)$$

(1) alcoxides (alcoholate) get hydrolyzed (2) or decomposed (3)

**Damaging process may progress rapidly and is accompanied by an increase in pressure due to hydrogen formation**

Alcoholate corrosion of Al

# Alcoholate (dry) corrosion of aluminum

## Technical temperature threshold

Influence of EtOH-content

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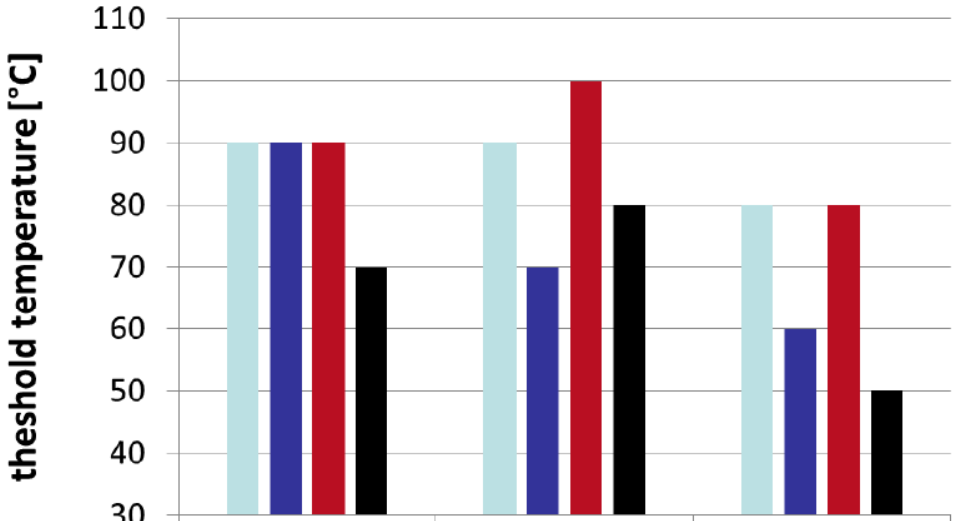


| | E10 | E20 | E85 |
|---|---|---|---|
| Al99,5 | 90 | 90 | 80 |
| AlSi9Cu3 | 90 | 70 | 60 |
| AlMn1 | 90 | 100 | 80 |
| Alusil | 70 | 80 | 50 |

**Observations:**

- **Al99,5 / AlSi9Cu3** drop of threshold with increasing EtOH-content
- **AlMn1 / Alusil** highest threshold for E20, lowest E85
- Lowest overall threshold for cast **Alusil / E85**

# Alcoholate (dry) corrosion of aluminum

## Technical temperature threshold

Influence of water-content

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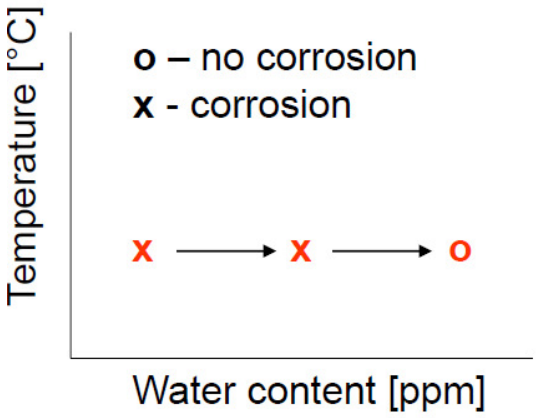
Starting temperature:

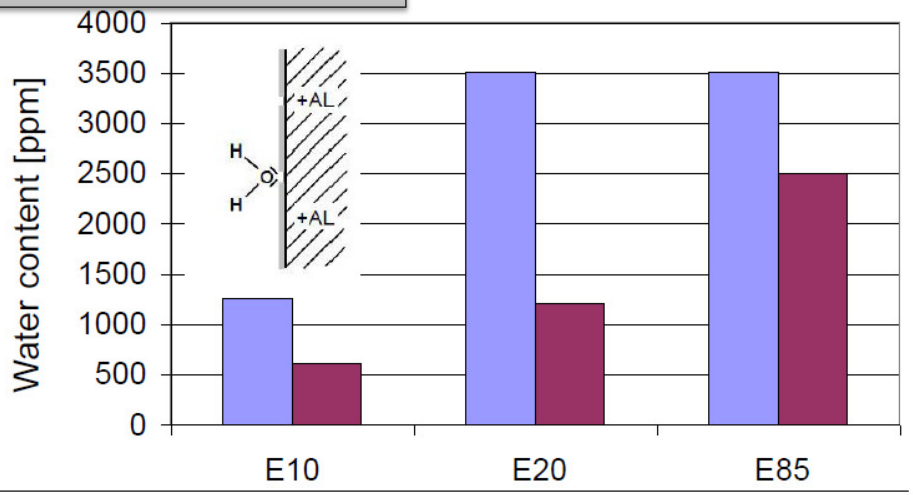
**10 °C above** the highest temperature level with **assured** alcoholate corrosion ➔ water addition, until no alcoholate corrosion occurs at this temperature level.

Starting temperature:

| Al99,5 | AlSi9Cu3 |
|---|---|
| E10: 130°C | E10: 120°C |
| E20: 130°C | E20: 110°C |
| E85: 120°C | E85: 100°C |

⇨ **Inhibition of alcoholate corrosion by water additions is possible, but....**



# *Effect of water on alcoholate corrosion*

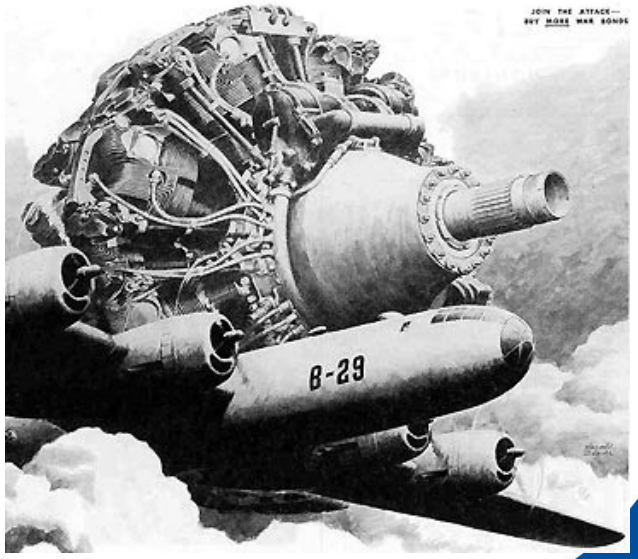
**A little water works as fluoride in toothpaste and avoids corrosion**

# *"Water Injection"*
# *70 years proven technology!*

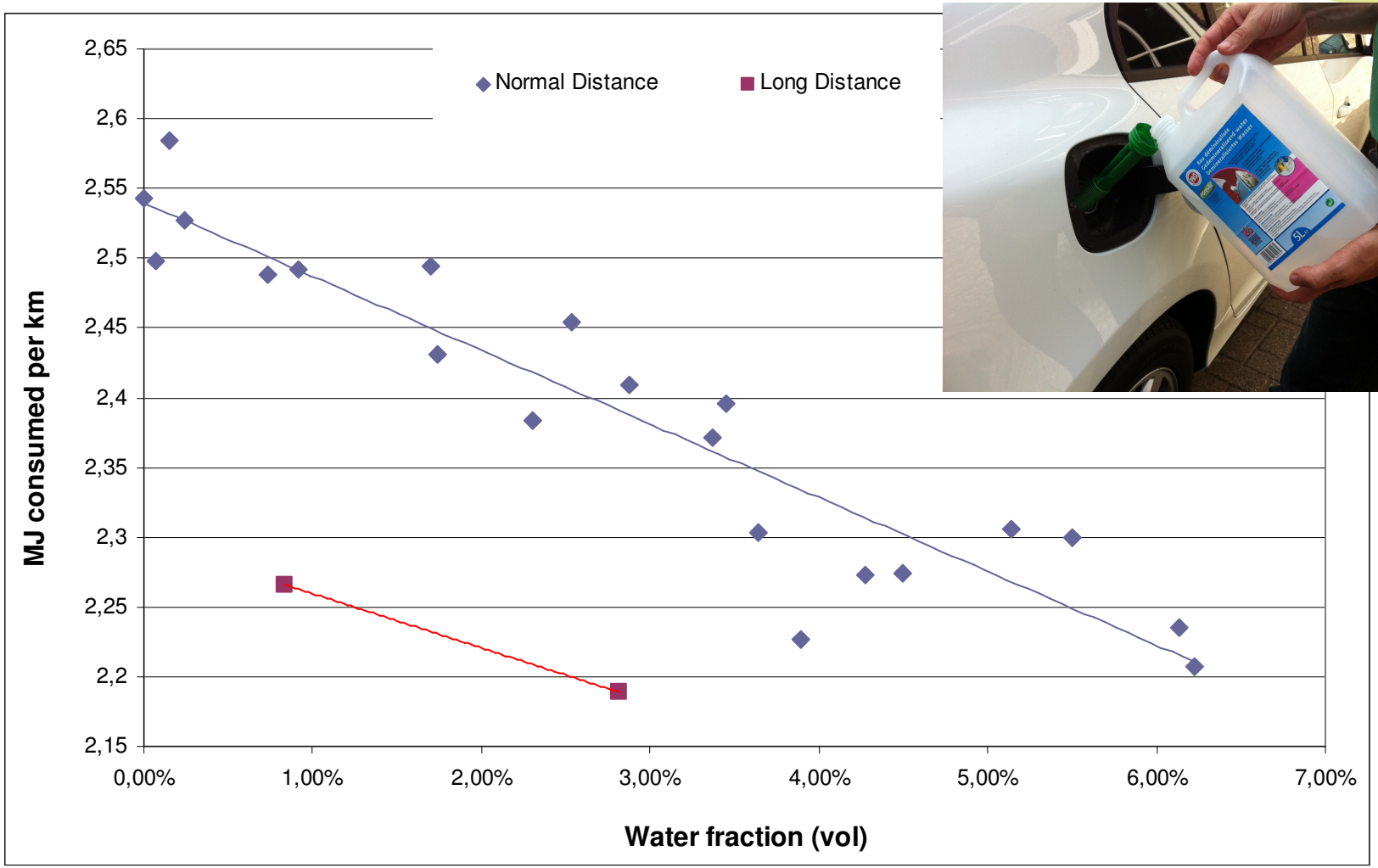
2010


1983

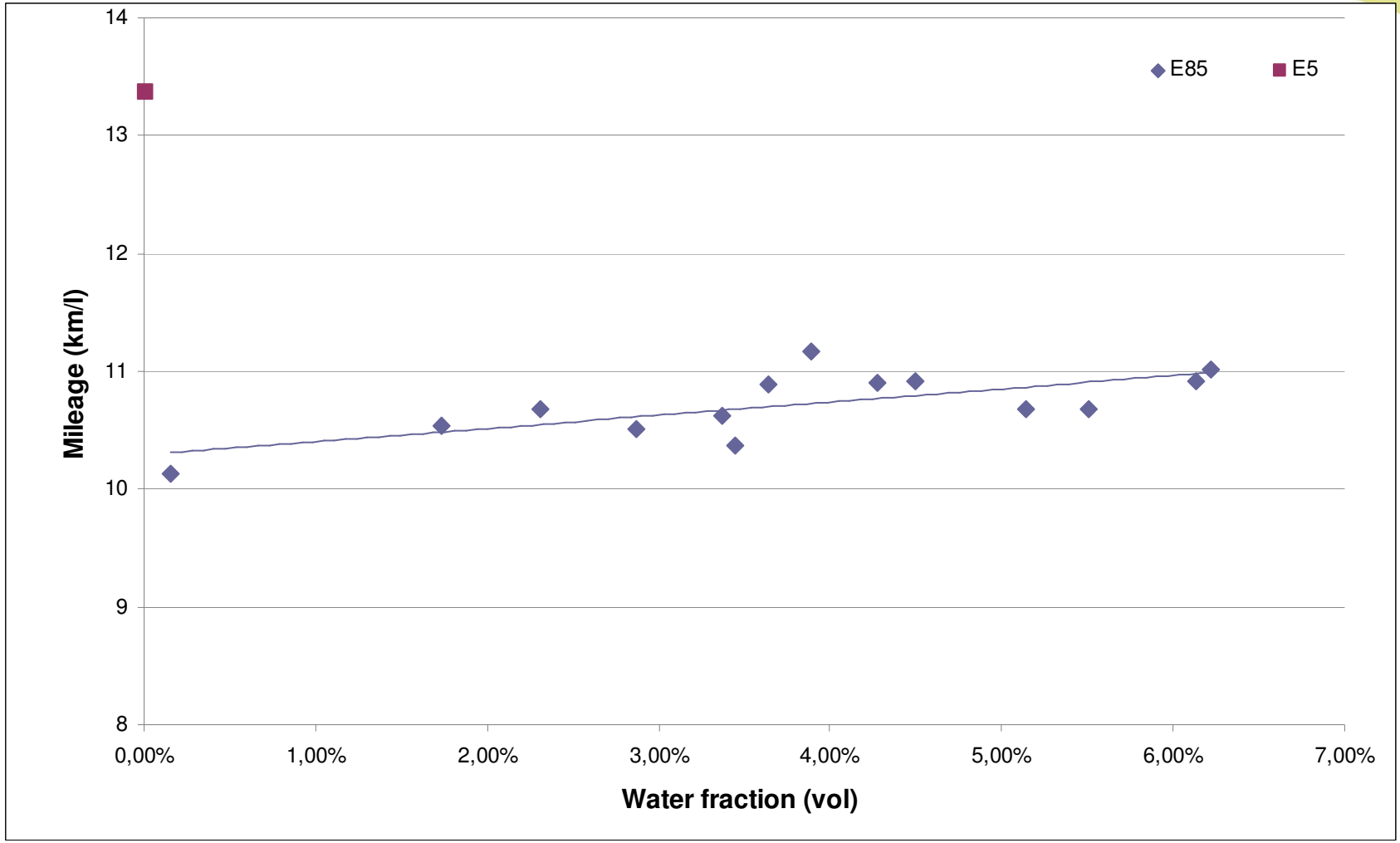

1940's



# Energy efficiency in a modern down sized turbo charged Volvo S60 T4F (Flex Fuel Vehicle)



# “Water injection” effect on mileage



# Hydrous E15 (hE15) sold at public pumps in the Netherlands since 2008

# Revision of Hydrous ethanol standard (NTA 8115) for E10+ blending

| Property | Unit | Limits | | Test method [a] |
|---|---|---|---|---|
| | | Minimum | Maximum | (See Clause 2. Normative references) |
| Ethanol content | % (*m/m*) | 93,0 | | EN 15721 |
| Methanol content | % (*m/m*) | | 0,5 | EN 15721 |
| Water content [b] | % (*m/m*) | at 2% | 6,1 | EN 15489<br>EN 15692 |
| pH [c] | | 6,0 | 8,0 | EN 15490<br>ASTM D 6423<br>NBR 10891 |
| Total acidity (expressed as acetic acid) [d] | mg/l | | 40<br>or<br>30 [d] | ASTM D 1613<br>EN 15492<br>NBR 9866 |
| Electrical conductivity [e] | µS/cm | | 3,5 | EN 15938<br>ASTM D 1125 |
| Appearance | | Clear and bright | | Visual inspection [f] |
| Inorganic chloride content | mg/kg | | 1,0 | EN 15492 |
| Sulfate content | mg/kg | | 4,0 | EN 15492 |
| | | | | |
| Phosphorus content [g] | mg/kg | | 0,2 | EN 15487<br>EN 15837 |
| Involatile material content [h] | mg/100ml | | 5 | EN 15691<br>NBR 8644 |

# Conclusions

- E10 in the US is probably less corrosive than E10 in Europe due to a higher water content in the ASTM D 4806
- We need a minimum water content in the fuel ethanol for direct blending of E5, E10 and higher blends to avoid alcoholate (alkoxide) corrosion.
- We also need to set a maximum water content for E5, E10 and higher blending applications to ensure that we do not run into phase separation issues.
- More hydrous ethanol blends do not pick up more contaminants. They are less hygroscopic and part of the overall water tolerance is already filled up with clean distilled water.
- Water injection has a positive effect on the Well to Wheel energy efficiency and reduces overall emissions.