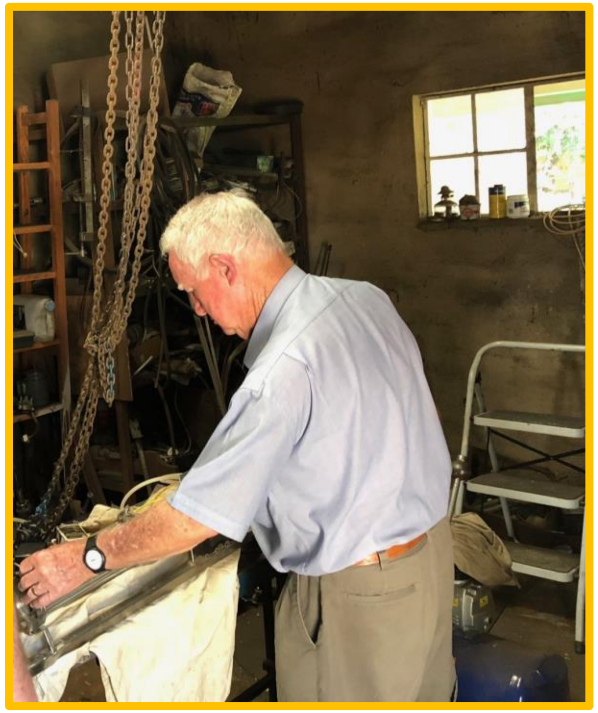
Novel oils and paints for the Energy Sector in the 21st Century

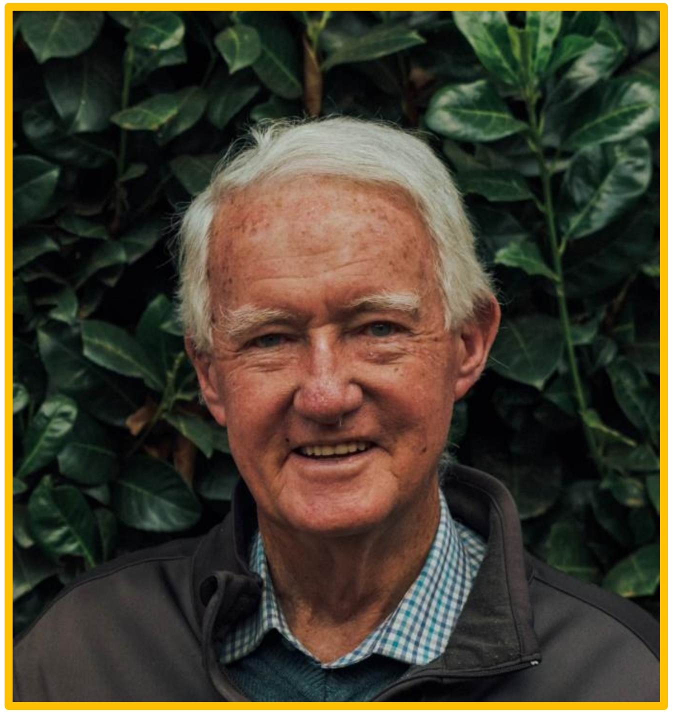
Dr Amanda Quadling (nee Seggie), FIMMM, CSci



Richard Seggie Memorial Lecture

November 2023

OCCA
The Oil & Colour Chemists' Association



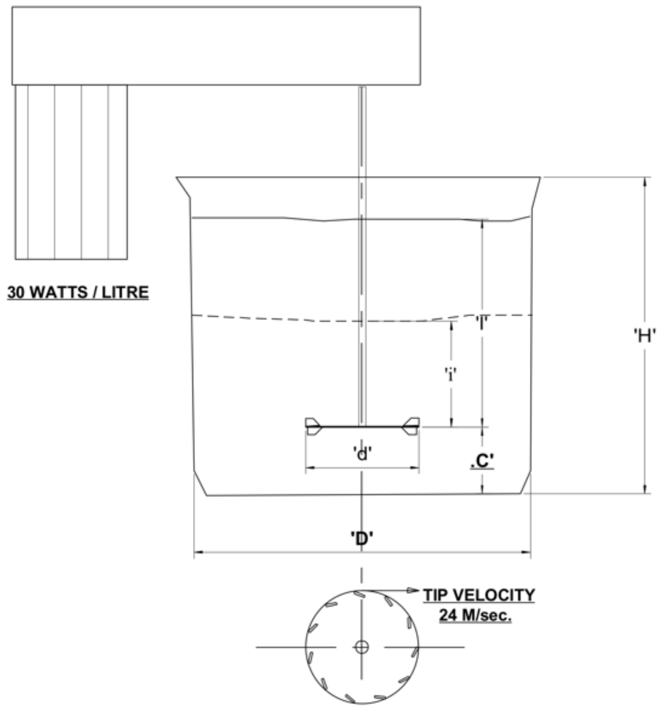
A decade ago…

Mechanical requirements for the incorporation of fillers

Richard Seggie
Technical Consultant
Jones Industrial Machinery

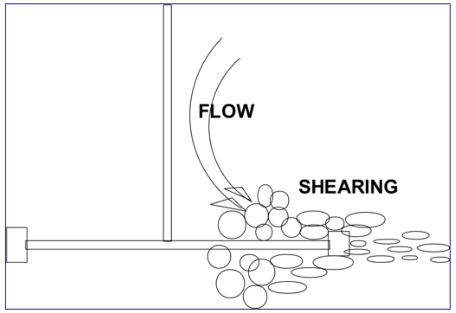
OCCA Mini-Symposium
October 2013

Tank dimensions	H	=	1.1/4 x D
Impeller diameter	d	=	0.1/3 x D
Tank diameter	D	=	3 x d
Impeller off the bottom	C	=	2/3 x d
min.-			
Product depth over impelleri		=	1 x d min.
Product depth over impellerI		=	2 x d max.
Impeller velocity at tip	V	=	24 m/sec.
Motor power	W	=	30 / litre



1 - Shearing

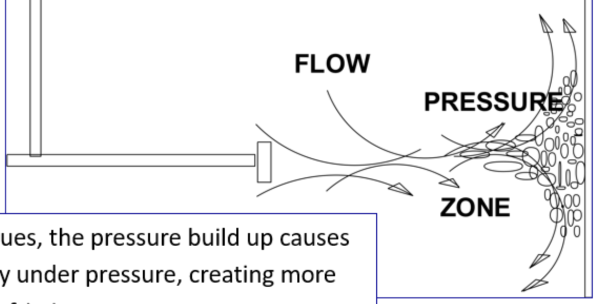
Where the friction induced by high velocity movement off the tip of the impeller tears the aggrlomerates apart.



2 - Attrition

1. Where the product is impelled off the periphery of the dispersion impeller at such a velocity that it continues to move at high speed until it hits the side wall of the tank and is stopped dead.

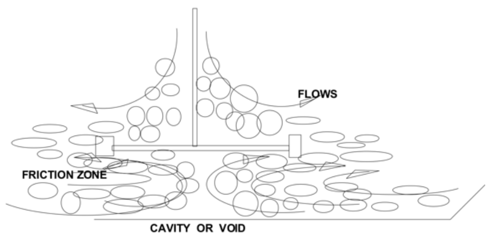
2. The following agglomerates travelling at the same velocity collide into the stationary particles and cause an attrition zone.



3. As the process continues, the pressure build up causes the mass to move away under pressure, creating more friction.

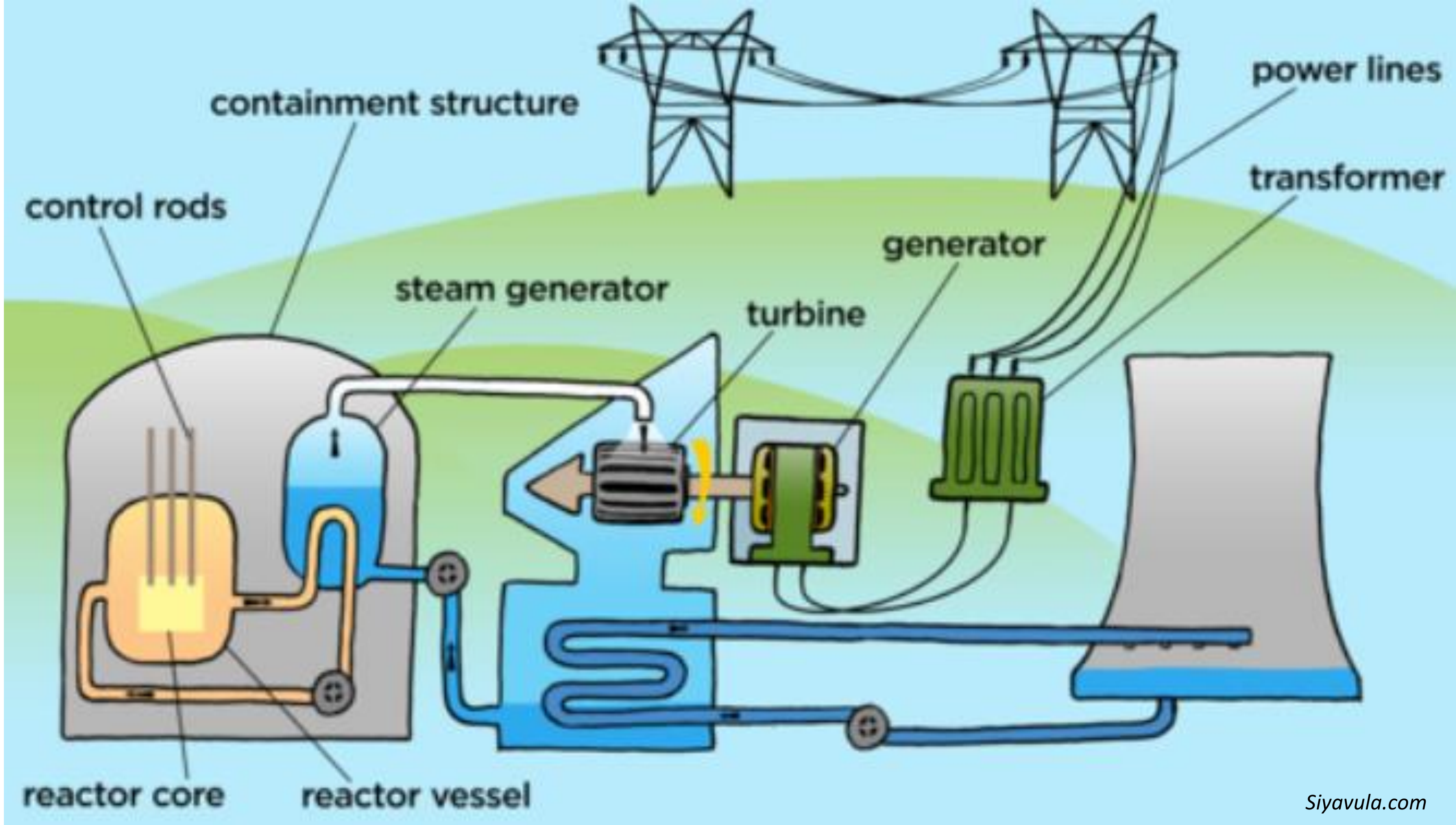
3 - Cavitation

- Where the product has been moved off the impeller at high speed the void left behind must be filled at an equivalent speed.
- The inrush of product to fill the void causes another friction zone against the outflowing product.



Agenda

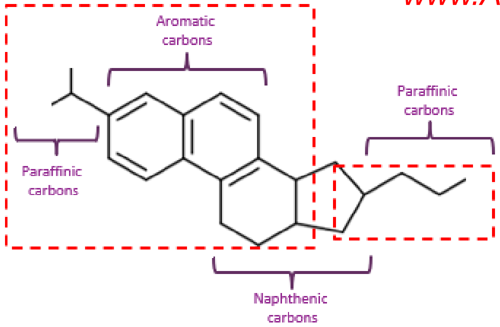
- DIELECTRIC 'OILS' for GRID TRANSFORMERS
- NUCLEAR POWERPLANT PAINTS



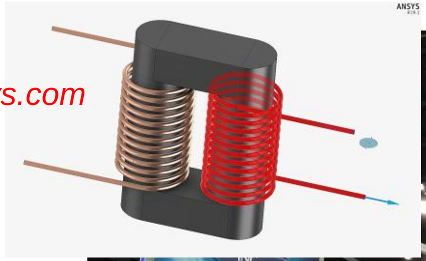
DIELECTRIC ‘OILS’
for Traditional Grid

MINERAL OILS are used as DIELECTRICS in Transformers on the Grid

CRUDE OIL is split by heat and distillation into LIGHT HYDROCARBONS (petrol and fuel) and HEAVY HYDROCARBONS (bitumen and base oils). Then further refinement proceeds:



www.Ansys.com

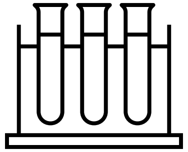


www.Delta.com

Group	Production route	Products differentiated by viscosity and sulphur and saturates contents	Category
I	Made by solvent refining	Petroleum base oil	Paraffinic
II	Made by partial hydrogenation	Cleaner petroleum base oil	Paraffinic
III	Made fully by hydrocracking	Best grade of petroleum base oil (sometimes called synthetic oil)	Paraffinic
IV	Synthetic oil	PAO – poly alpha olefin	Paraffinic
V	Made by distillation and raffination	Naphthenic oils and esters	Naphthenic

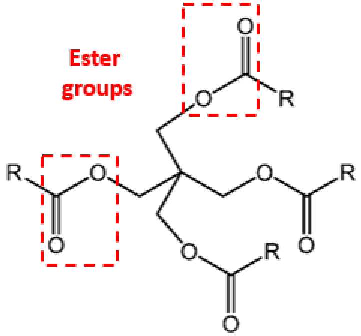
- **A dielectric is a material that stops electrical arcing – it's often an oil**
- **In a transformer (which steps voltage up or down in the electricity grid), arcing between the coils must be prevented to ensure fire safety**

ESTERS are the new DIELECTRICS in Transformers on the Grid



Alcohol (R’ – OH) reacts with acid (OH – R = O) to form ester O = R – OR’, while releasing water.

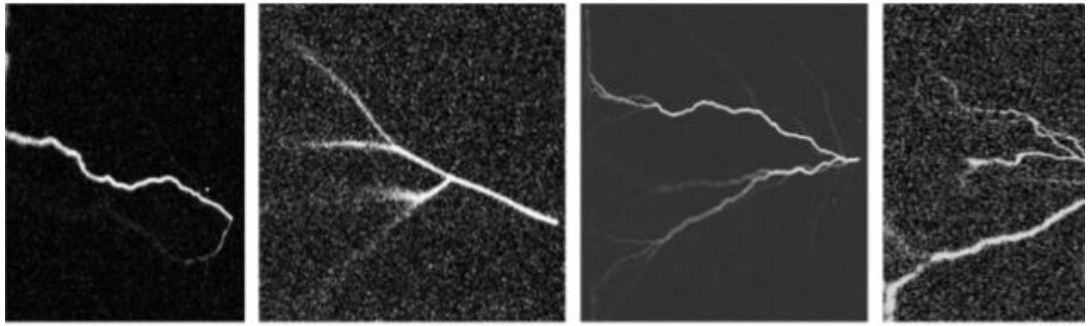
- The concentration of ester groups in the final ester chemical, determines its polarity.
- There is a small permanent dipole moment in the ester because of the unsymmetrical electron density around the carbon – oxygen bonds.



	MONO ACID	DI / POLY ACID
MONO ALCOHOL	Mono ester	Di ester
DI / POLY ALCOHOL	Polyol ester	Complex ester

- **Before WWII, polyol esters were developed using neopentyl / polyols (e.g. pentaerythritol) + short chain natural fatty acids (C6-C12). These provide high stability base fluids.**
- **During WWII, diester fluids were developed using adipic acids + oxo-alcohols (raws no longer available) for aircraft engine and hydraulic oils.**

Electrical Engineering Dept, Uni Manchester



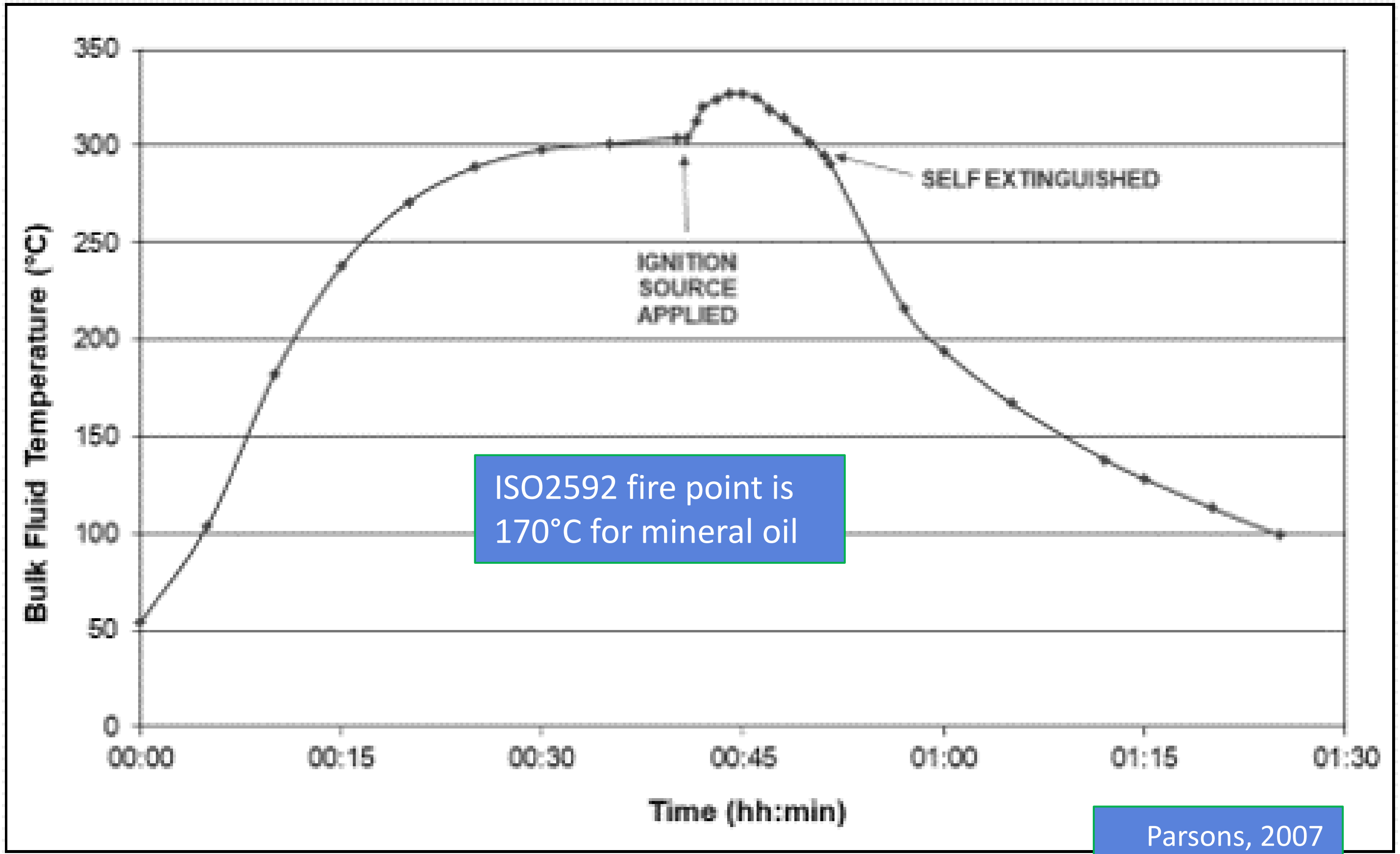
(c) (d) (e) (f)

Key uses	Properties that are important
Aviation	Thermal stability
Automotive	Seal swell, solvency, lubricity
Mobile hydraulics	Oxidation stable but biodegradable (i.e. low environmental impact)
Railway / marine	
Refrigeration	Neopentyl esters are compatible with HFC’s in compressors

ESTERS can be naturally derived or industrially synthesized

… but both offer natural benefits which include higher fire points (>300°C) compared to traditional dielectric liquids

Low calorific content of esters means that when eventually they burn, the heat released is inadequate to maintain a liquid pool temperature above the fire point



MIDEL 7131 test in small fire point test cup

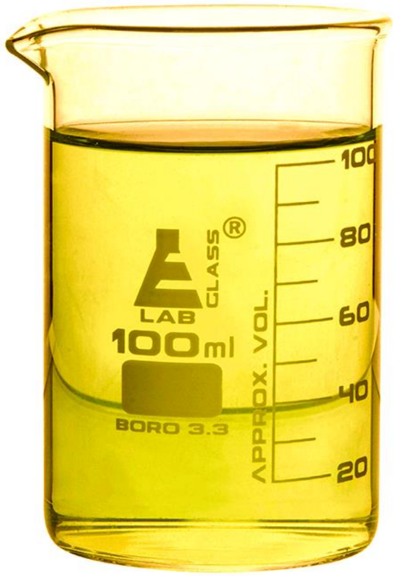
Parsons, 2007 for M&I Materials

Some ESTERS oxidise, which affects choice of application

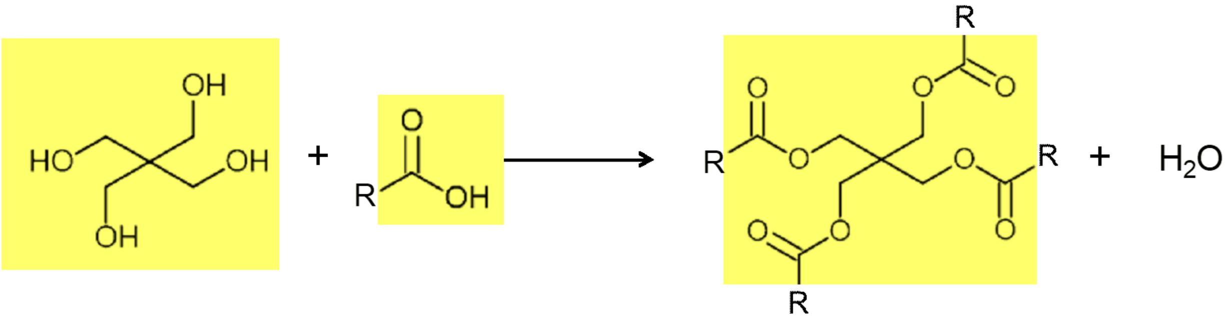
Natural esters oxidise in air, especially at increased temperature (double bonds get broken)

- **Acidity increases**
- **Viscosity can increase**
- **Gelling can occur from surface layer cross-linking**

Lack of double bonds, make **synthetic esters stable under oxygen** with no cross-linking / gelling



Esters don't contain the sulphur-containing contaminants which mineral oils often have -> less need for **metal passivators** to prevent reactions with copper windings and the consequent corrosive copper sulphide formation.

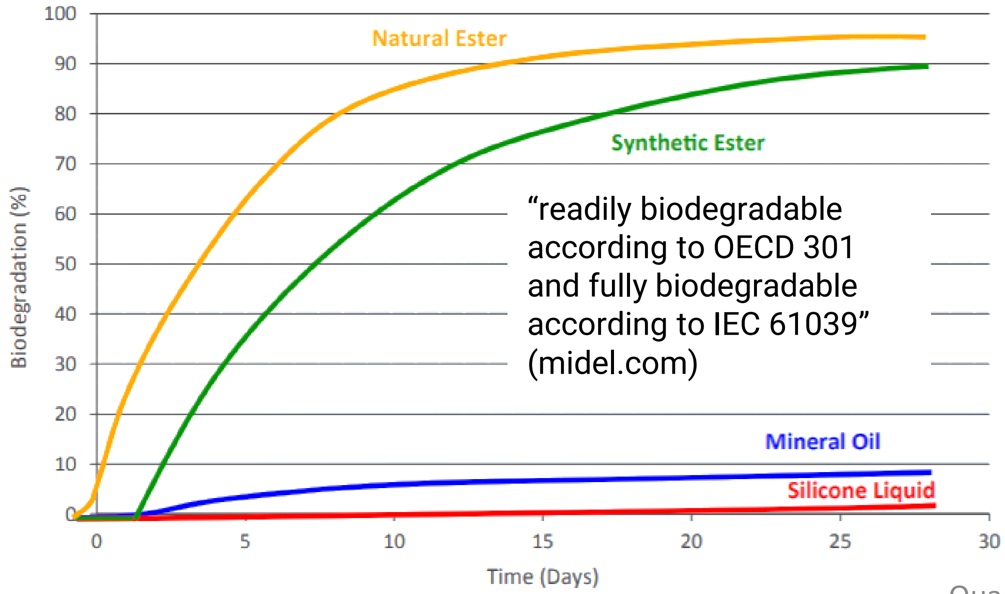


R= Saturated alkyl group

ESTER products can be carbon neutral

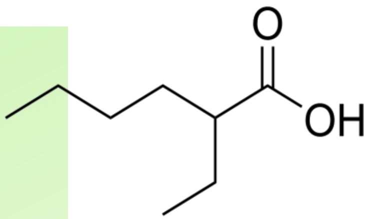
Canola is a natural source of ester ‘oil’ and favoured relative to palm or soya derived liquids from a food security perspective

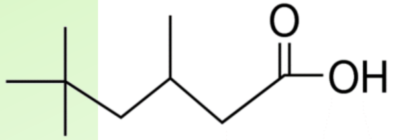
… because of agricultural derivation, and biodegradable because of their molecular characteristics

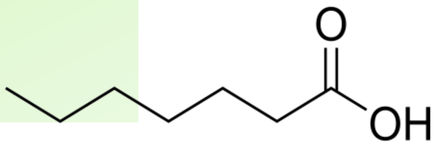


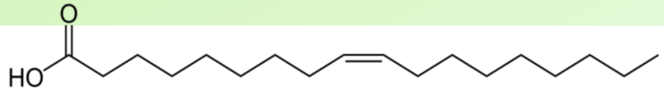
Biodegradability increases with

1. Decreasing inhibition of ester hydrolysis
2. Reduced branching (branching reduces β-oxidation)
3. Degree of saturation in the molecule
4. Reduced molecular weight of the ester









ESTERS exhibit high water saturation characteristics

… improving the longevity of transformer life (paper insulation survives longer) and reducing bubble-triggered breakdown under high voltages. Polyol esters typically have long chains and branching, bringing steric effects which reduce hydrolysis.

Cellulose degradation occurs because of:

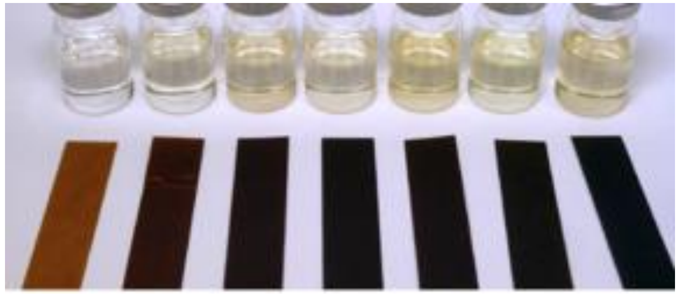
- Oxidation: cellulose oxidation produces water and CO_2 via a sequence of intermediate species (and some radicals)
- Pyrolysis: occurs at high temperatures (when transformer overheats for example)

Cellulose degradation can be monitored through the product species (furans or, increasingly, methanol)

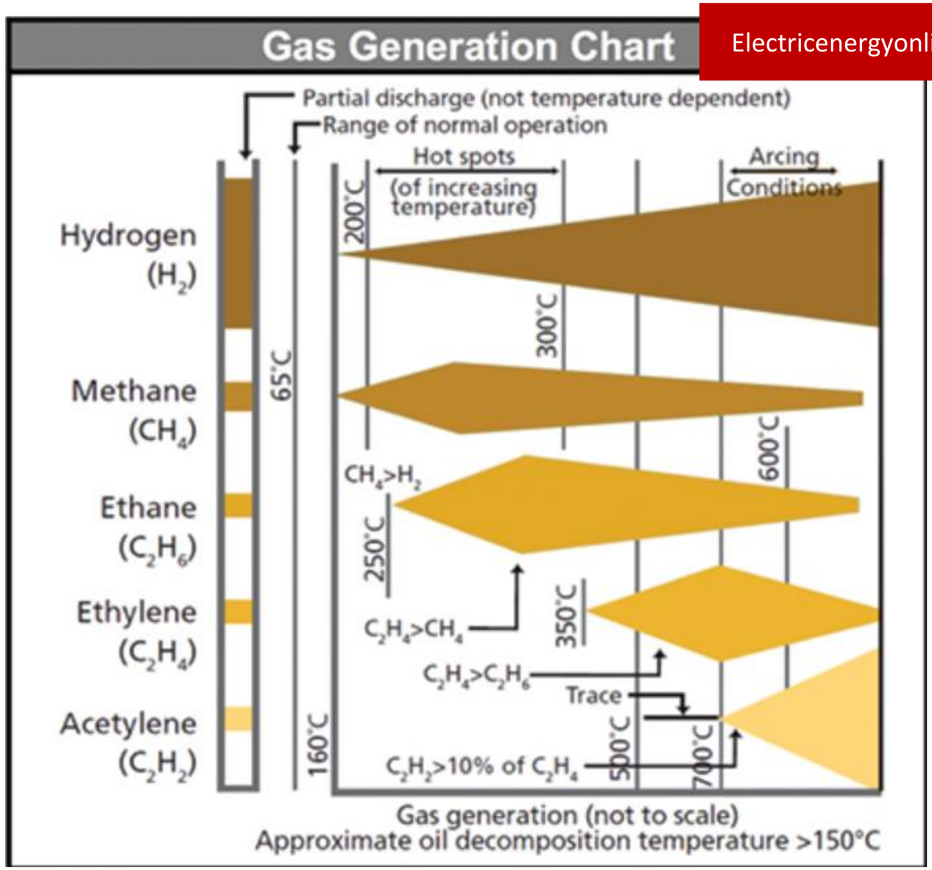
Use of ESTERs means redefining the transformer health test tools

… mainly dissolved gas analysis (DGA) which identifies dielectric breakdown products

Utility companies now run accelerated ageing tests at above-average operating temperatures to estimate transformer life extension through improved paper performance



R. Braezeal, pers comm, Southern California Edison, 2019



Electricenergyonline.com

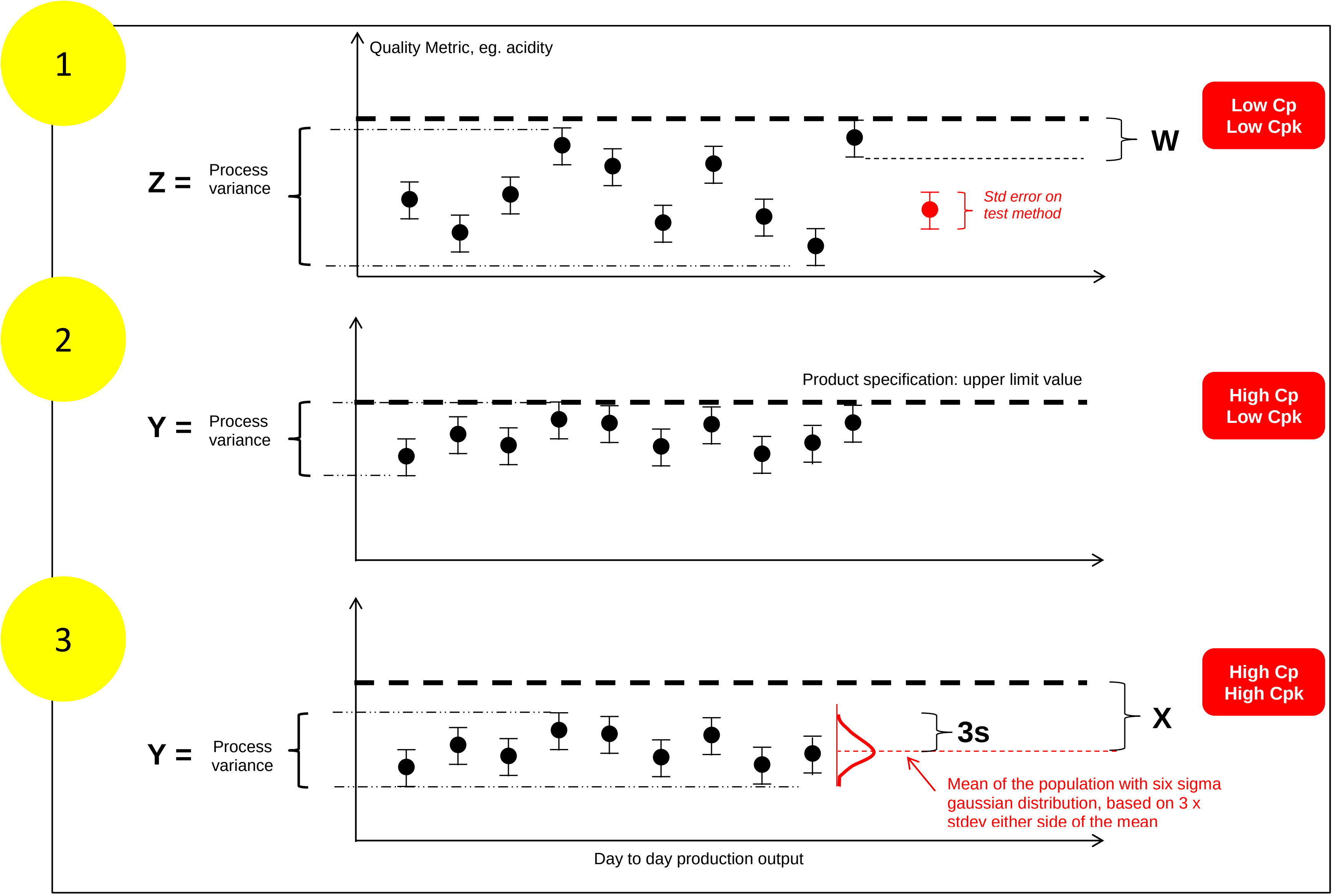
Dissolved gas analysis has become an established assurance tool for transformer health, based on mechanistic understanding of the gas products of various electrical activities across a span of operating temperatures

ESTERS quality control is highly sensitive re tan delta (dielectric dissipation factor)

Cp – the process potential index – **degree of variance** in a manufactured population of samples. High variability (range Z in Scenario 1) is less desirable than more consistent production (range Y in Scenarios 2 and 3).

Cpk – the process capability index – **degree of variance** in a manufactured population of samples **AND how far inside target specification**, the manufactured population is.

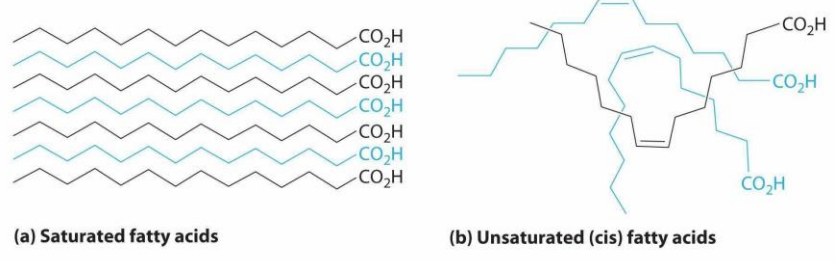
Ester properties are extremely sensitive to transport and storage conditisions ((UV exposure, moisture) so that manufacturing release thresholds have to be tighter than the IEC standards to comply with QA targets at customer receipt end…

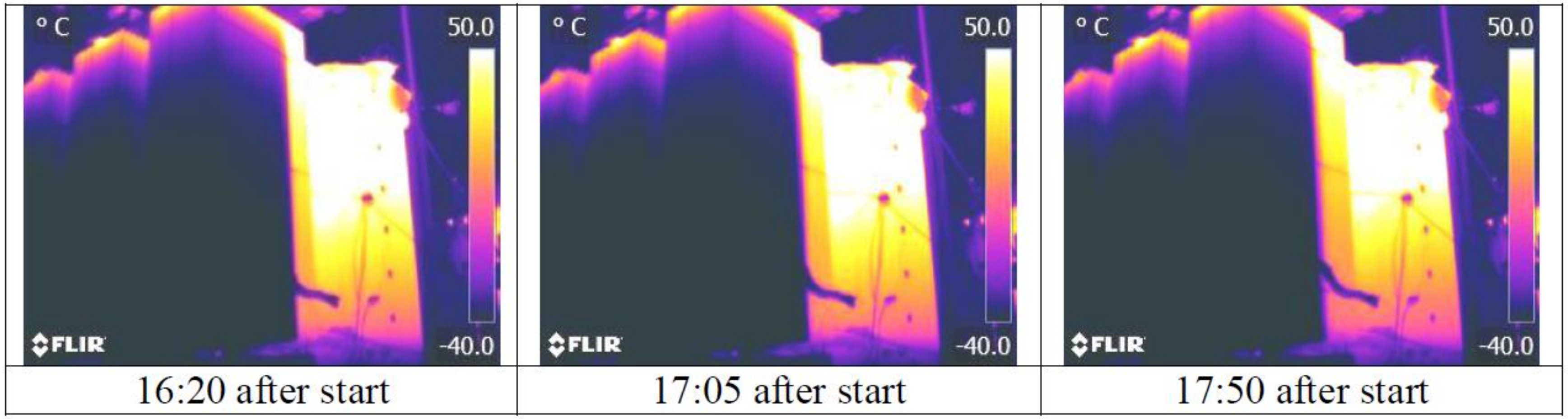


ESTERS allow transformers to work in cold climates

- **Soya based** ester liquids have a pour point around -18°C and **canola based** esters around -31°C
- **Viscosity rises** when the liquids are held at temperatures below -10°C -> risk of solidification -> less effective cooling around hot spots (heat trapped in the windings)
- As **risk mitigation, transformers can be started ‘off load’** while blocking the radiators or adding initial external heating to elevate liquid temperature.
- **Synthetic ester** operates in both breathing and sealed transformers at temperatures below -50°C.

https://www.quora.com/What-is-the-relationship-between-degree-of-unsaturation-and-melting-point-for-fatty-acids





Pour point

For natural esters, introducing unsaturation causes more bends in the hydrocarbon chains which inhibits packing of molecules and lowers the pour point.

Viscosity

Bends in the hydrocarbon chains result in more friction as a molecules slide by one another, increasing viscosity.

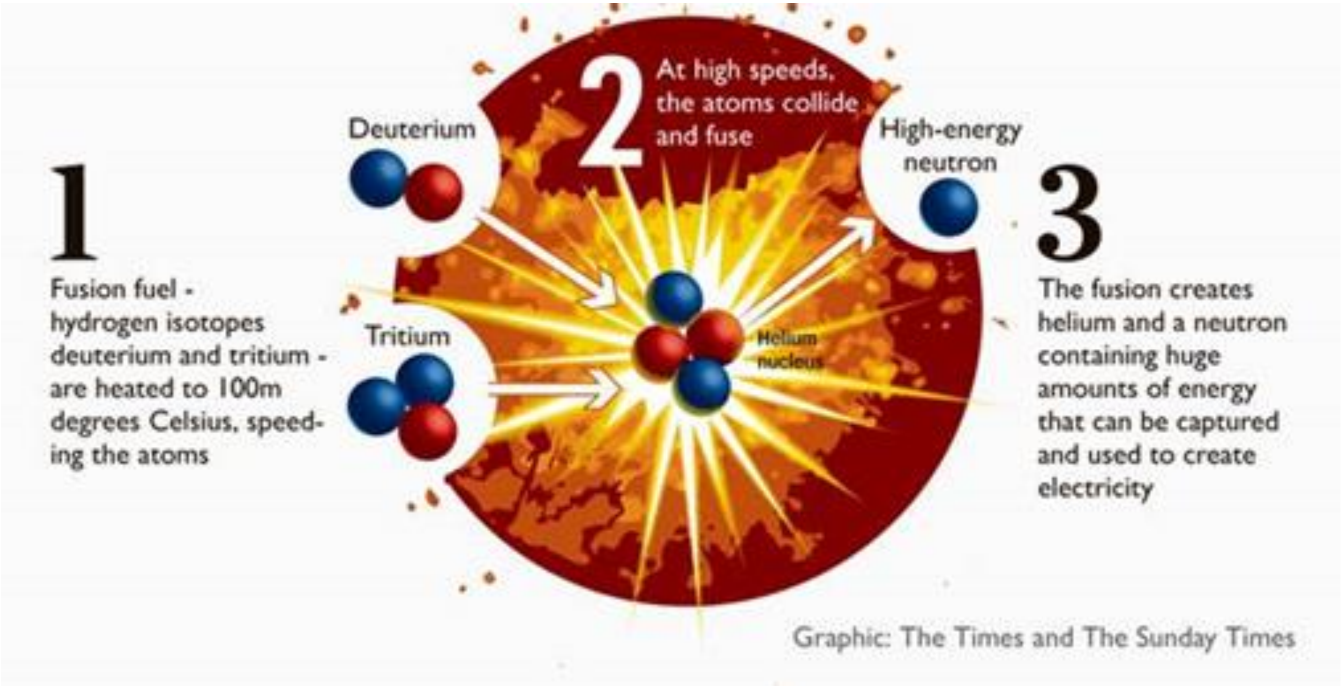
Siemens’ cold start investigation (55 kV auto-transformer) at full load, then at low load at temperatures of -40 ^{o}C and -50 ^{o}C

- In both cases, hot spot temperature did not exceed critical levels specified by the IEC 60076 standard
- Some radiators were active; others still at ambient temperature of -40 ^{o}C up to 14 hours after start

F. Bachinger and P. Hamberger, "Measurement of thermal behavior of an ester-filled power transformer at ultra-low temperatures," *Elektrotechnik und Informationstechnik*, vol. 135, no. 8, pp. 536-542, 2018.

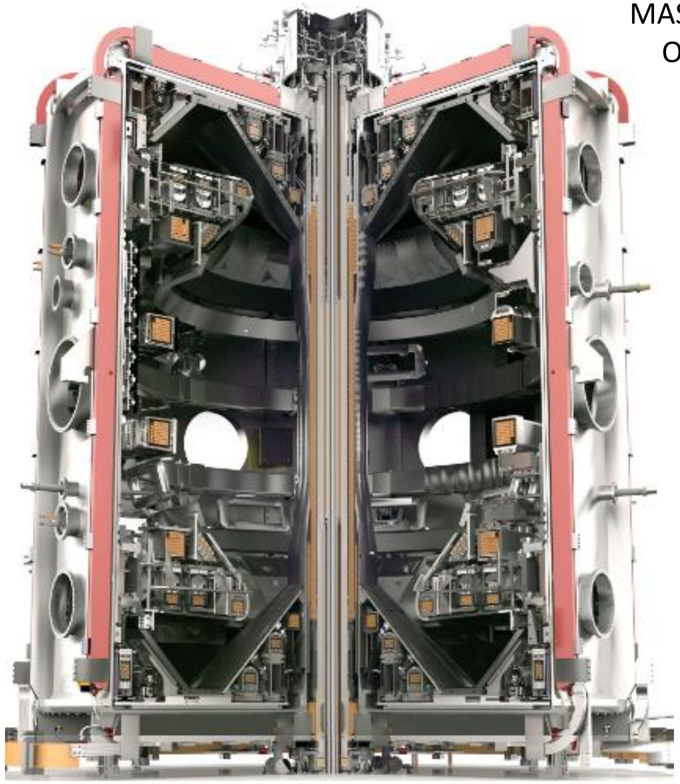
PAINTS and COATINGS for Nuclear Powerplants

Fusion is clean, low carbon next generation nuclear energy



Magnetic confinement fusion happens in a tokamak

MAST-U at UKAEA in Oxfordshire, UK



- Fusion occurs when hydrogen isotopes are CONFINED enough to combine to form helium, releasing a neutron with lots of energy
- The neutrons are sent through lithium, creating new tritium + extra neutrons + heat

UK, USA, EUROPE, S.KOREA are all planning fusion powerplants..

Paints / coatings are used in nuclear powerplants to …

1 – protect against corrosion (pipe/ plant breaches risk leaking radioactive liquid; creation of debris might clog emergency system pumps)

2 – enable easy decontamination of radionuclides /tritium from walls and floors

3 – protect against wear

4 - prevent ingress of radioactive dust and permeation of radioactive condensate

Coatings are considered "qualified" if they maintain adhesion under simulated post LOCA conditions

Olkiluoto-3
Nuclear powerplant in Finland
(teknos.com)

The application includes multiple environments and substrates

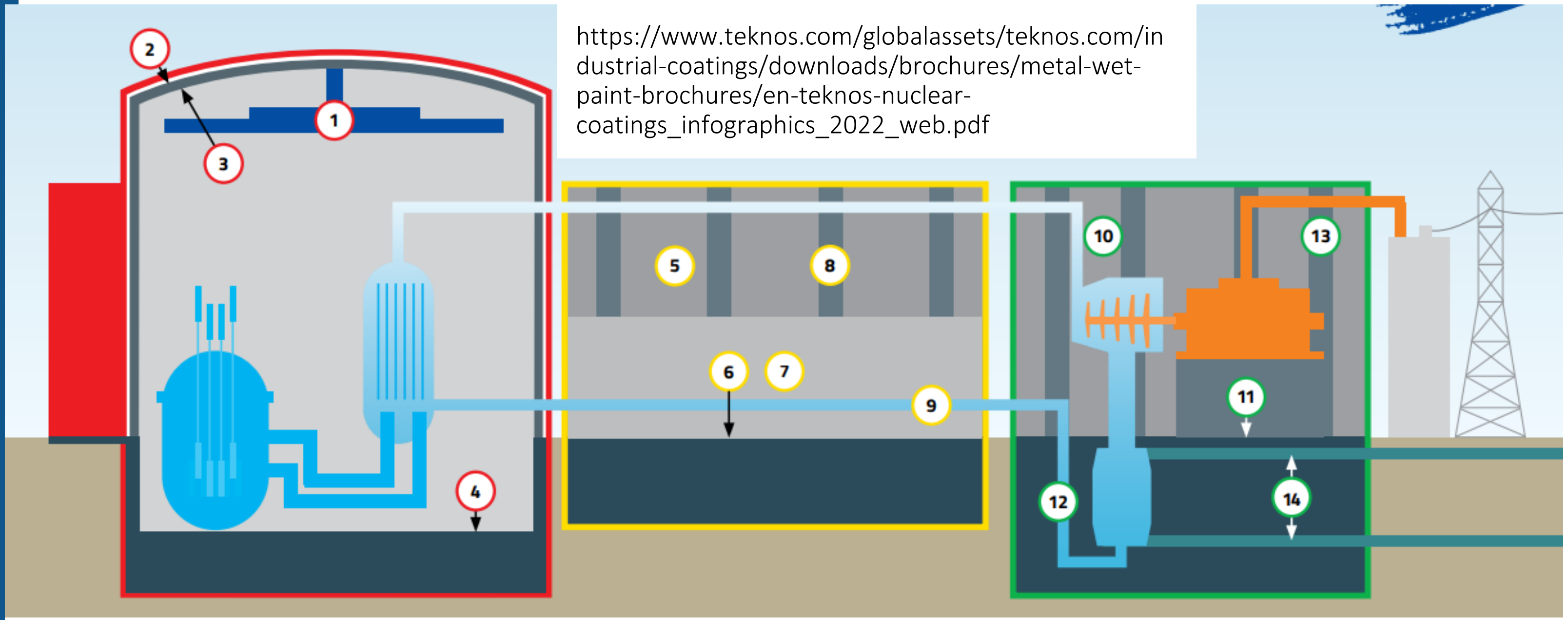
In pressurized water reactors, for example, coatings are applied to

- Reactor building liner
- Structural steel
- Steam generator support steel
- Gallery steel and crane
- Uninsulated equipment surfaces and piping
- Concrete surfaces inside the reactor

Layered approach taken:

Topcoat, primer, surface coating

To address multiple risks (and local failures of cross-linking for example..)



https://www.teknos.com/globalassets/teknos.com/industrial-coatings/downloads/brochures/metal-wet-paint-brochures/en-teknos-nuclear-coatings_infographics_2022_web.pdf

Dedicated accreditation routes and standards

- **ISO 8690** (Decontamination of radioactively contaminated surfaces. Method of testing and assessing the ease of decontamination)
- **STUK-YTO-TR 210** (Requirements of Finnish Radiation and Nuclear Safety Authority)

American National Stds Institute ANSI N101.2, N101.4	Used where	Coating performance
Service level 1	Inside reactor containment	Coating failure mustn't impact impair safe shutdown via post-accident fluid systems
Service level 2	Outside reactor containment but subject to radiation exposure / radionuclide exposure	Coating should not present normal operations
Service level 3	Outside reactor containment	Might adversely affect safety functions of systems and structures
American Society Testing and Materials		
ASTM D 5144-00	Standard Guide to Use of Protective Coatings Standards in Nuclear Powerplants	
ASTM D 3843-00	Standard Practice for Quality Assurance for Protective Coatings Applied to Nuclear Facilities	

Guides YVL 4.1 and 4.2 issues to be addressed:

- Radiation resistance
- Ease of decontamination
- Chemical resistance
- Durability under operating conditions / accident conditions
- Fire technical properties


STUK

STUK-YTO-TR 210 / August 2004

REQUIREMENTS FOR COATINGS OF NUCLEAR POWER PLANT CONTAINMENTS

Eva Häkkä-Rönnholm
VTT Building and Transport

Image: teknos.com

Chemistry of nuclear coatings

Classification by chemistry	Typical type	Function / benefits
Epoxy	Glycididal ether (from bisphenol-A and epichlorohydrin); crosslinking of intermediaries aided with copolymer curing agents)	With phenolic modification, enhanced water resilience (with detraction of higher brittleness)
Alkyd	Mix of oil / fatty acide, dicarboxylic acide and polyhydric alcohol	Because of the drying oil, limited chemical / moisture resistance but lost cost, easy application and weather resistance
Inorganic zinc	Mix of zinc metal powder and inorganic silicate paint binder (solvent or water borne)	Galvanic protection to steels; high abrasion resistance but poor at extremes of pH (empirical evidence)

Commercial random examples
Amercoat 66 (Ameron), System KL9, KL10 Surfaces (Keeler & Long) for concrete, System S-1, S-10 Primers (Keeler & Long) for carbon steels
Amercoat 5105 (Ameron), Carbocoat 115 primer (Carboline)
Dimetcote 6 (Ameron), Carbozinc 11SG primer (Carboline)

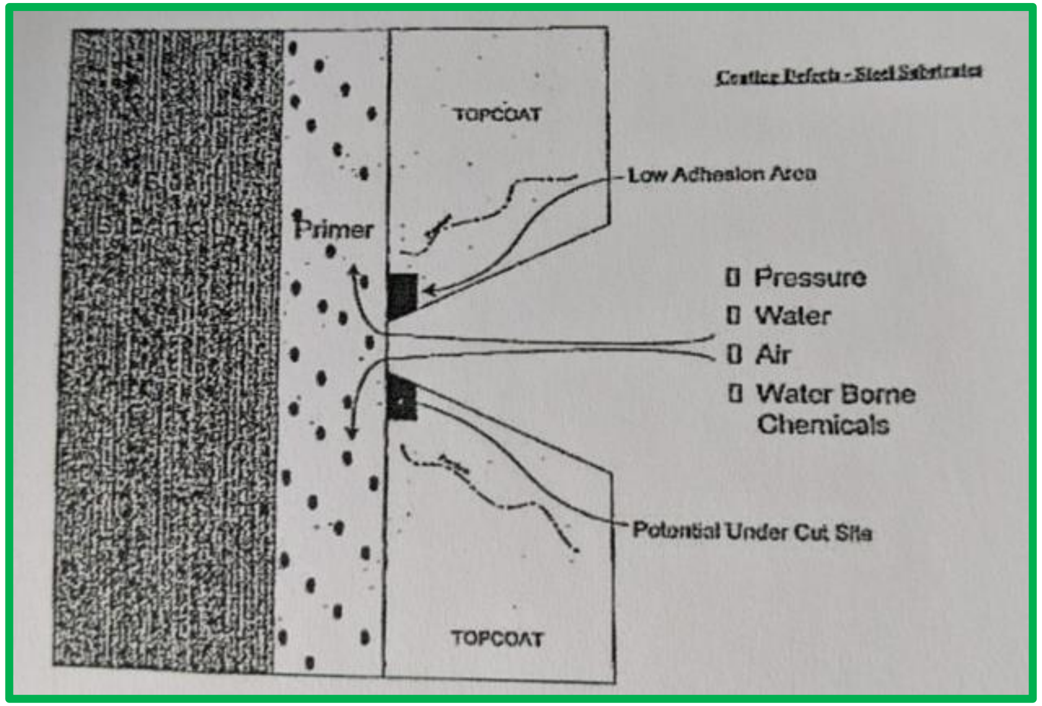
2005, Natesan and Natarajan: Survey on Leaching of Coatings Used in Nuclear Power Plants: Letter Report for Office of Nuclear Regulator (NRC Job Code N6100)

Degradation mechanisms are varied

Contaminant release from coatings occurs because of:

- Dissolution of minerals
- Adsorption (sorption control)
- Contaminant availability

Coating environment interaction s – example with steel (Sindelar et al. 2000)



With respect to concrete:

- Paints' alkali resistance prevents **reaction with alkali contract**
- Paints moisture resistance prevents **drawing of the natural moisture content** in concrete (strong adhesion will prevent blistering)
- **Crack bridging** required in coatings due to concrete evolution over time
- **Calcium carbonate build up** at concrete / coating interface also a challenge

- ❑ Paints tested in recirculating loops, blowdown tests, air-gamma irradiation, steam-gamma irradiation, autoclaves
- ❑ Coatings tested at 160°C up to 26 days
- ❑ Coatings tested at 2 x 10^8 rad in borated spray
- ❑ Delamination is common fail route..

Example of recent research - 1

In 2019, Argonne announced they'd developed a novel dual coating technique for nuclear fuel coating. The researchers used:

ALD to powdercoat (ZrN) fuel cladding; **delivered transparency to neutrons** (allowing them through to the fuel) but effective at protecting low enriched uranium fuel)

ALD to apply aluminium oxide to provide hardness and **wear resilience** (100x hardness improvement)

A combo of EPD/ALD combo to create **novel coating microstructure**

- ✓ Compact
- ✓ Ceramic
- ✓ Sticky (to the cladding)
- ✓ Irradiation resilient - survived heavy ion bombardment at Argonne's Intermediate Voltage Electron Microscope (IVEM) facility

Argonne NATIONAL LABORATORY

- **Atomic layer deposition** (closes pinholes enables very thin and dense layer laydown but slow)
- **Electrophoretic deposition** (deeper coatings and faster, but less dense)

https://www.anl.gov/education/argonne-discovery-offers-new-way-to-coat-nuclear-materials - 2019

Argonne's Sumit Bhattacharya (left) and Abdellatif Yacout (right) have discovered a new way to coat nuclear materials that support efforts to minimize use of high-enriched uranium. (Image by Argonne National Laboratory.)

Example of recent research - 2

Tokamak coolant facing alloys face flowing conditions, mechanical loading and radiation. Tests run here on self-passivating Al-based coatings on RAFM substrate (CVD and electroplated varieties) before and after strain.

Formation of intermetallics in the CVD coating led to crack failures. Electroplating looks more promising.

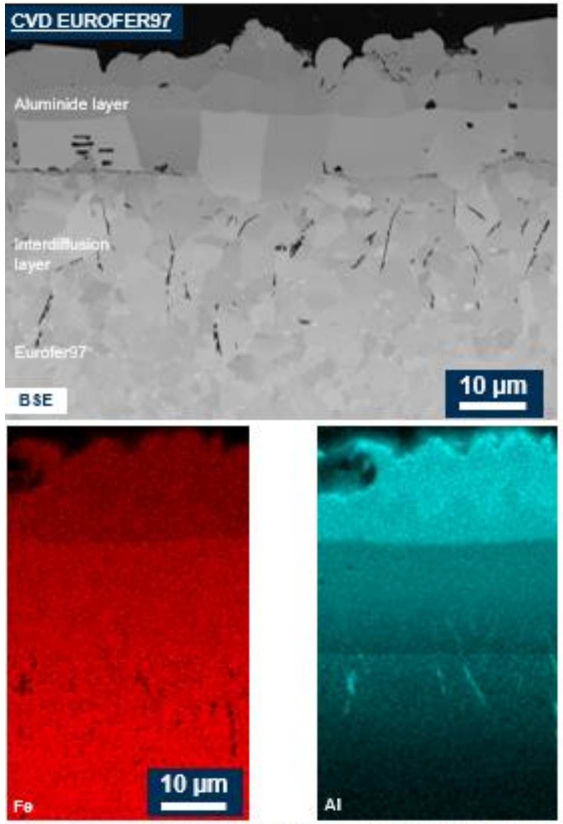
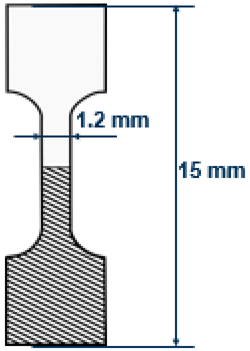


Fig. 7: BSE image of the near surface region of the CVD specimen, and associated SEM-EDX elemental maps.



SS-J3 dogbones strained at 10^{-3} s^{-1} under digital image correlation and then scanning electroni microscopy used to evaluate modified microstructures.

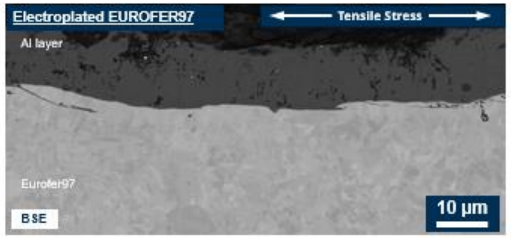


Fig. 5: Representative cross-section of the EUROFER97 coated with the electroplated Al-base coating after engineering straining at ≈1%.

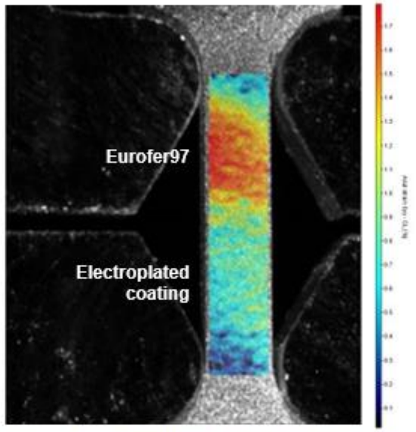


Fig. 4: Straining map for the electroplated specimen after ≈1% engineering straining.

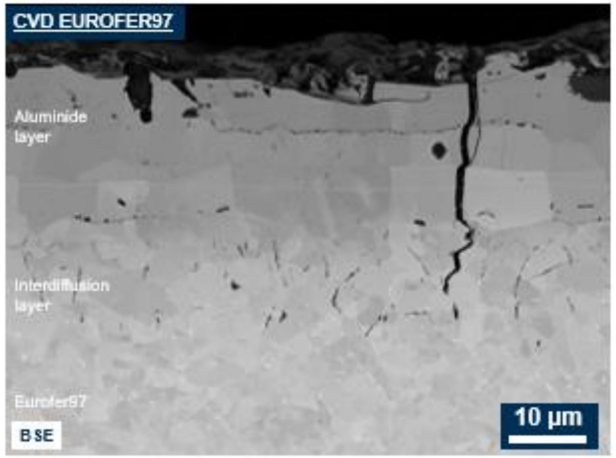


Fig. 10 ↑: Representative cross-section of the cracked EUROFER97 coated with the CVD Al-base coating after engineering straining at ≈1%.

Volpe et al., 2023, UKAEA

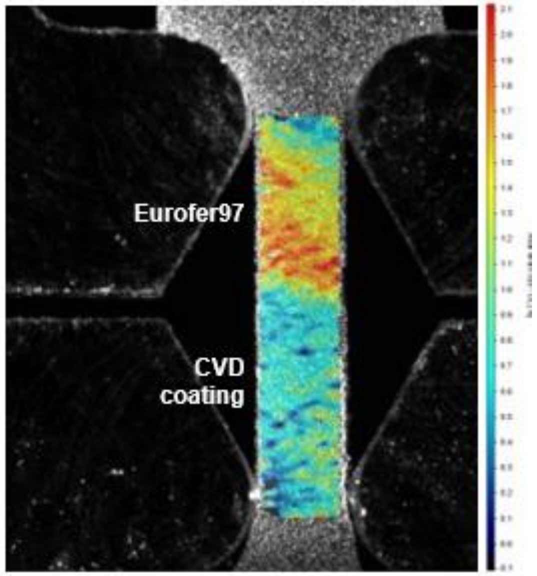


Fig. 9: Straining map for the CVD specimen after ≈1% engineering straining.

Thank you for listening

Amanda Quadling

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De Beers – LAB MANAGER

BHP Billiton – PROJECT MANAGER

SA Science Council – DIVISION MANAGER

Morgan Advanced Materials – RESEARCH DIRECTOR

M&I MATERIALS – TECHNICAL DIRECTOR

UK ATOMIC ENERGY AUTHORITY – EXECUTIVE DIRECTOR

1992 BSc Geology Chemistry — UNIVERSITY OF THE WITWATERSRAND, JOHANNESBURG

1998 BTh Ethics — UNISA university of south africa

2003 MSc Housing — LSE

2015 PhD Materials Science — Imperial College London