Corrosive Sulfur in Transformer Insulating Mineral Oil: What is it and how to prevent the Adverse Effect

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Fabio Scatiggio was born in Venezia, Italy, in 1957. He is with Terna Rete Italia where he is in charge as Chemical Laboratory Manager.

He is the Italian representative in many IEC TC 10 and CIGRE A2&D1 working groups. Mr. Scatiggio has published many papers on transformers diagnosis by DGA and on problems related with presence of corrosive sulphur in oil.

Mr. Scatiggio received the “IEC Award 1906” in 2008 and was awarded as “CIGRE Distinguished Member” in 2012.

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Historical background

The term of corrosive sulfur identifies those forms of sulfur that are corrosive under normal operating thermal conditions of the transformers.

Some of sulfur compounds are beneficent to the oil because they act as retardants or passivants in the oxidation process (“good sulphur”)

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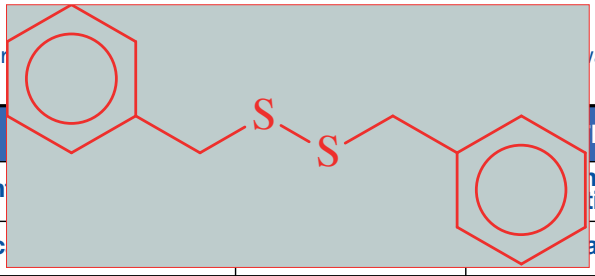
Historical background

Not all the sulfur



way

		IVITY
Elemen		high tive
Merc		active
Sulphides (thioethers)	$R\text{-}S\text{-}R_1$	reactive
Disulphides	R-S-S-R	stable/reactive
Thiophenes	5 membered ring with S	very stable

Table from: Lance R. Lewand "The Role of Corrosive Sulfur in Transformers and Transformer Oil" - Proceedings of the Sixty-Ninth Annual International Conference of Doble Clients, Boston, MA, USA, 2002.

Test Methods

International standard organizations have adopted, since the '50s, a simple ON/OFF test to detect the corrosiveness of the oils

Method	Description
ASTM D130 – IP 154 – ISO 2160	COPPER STRIP AT 100°C
ASTM D1275/A - ISO 5662 - NBR 1505	COPPER STRIP AT 140°C FOR 19 HOURS
DIN 51353	SILVER STRIP AT 100°C FOR 18 HOURS
TERNA (Extended ASTM D1275)	COPPER STRIP AT 140°C FOR 48 OR 72 HOURS
DOBLE - ASTM D1275/B	COPPER STRIP AT 150°C FOR 48 HOURS
CCD (Covered Conductor Discoloration Test) IEC62535	COPPER AND PAPER STRIP AT 150°C FOR 72 HOURS

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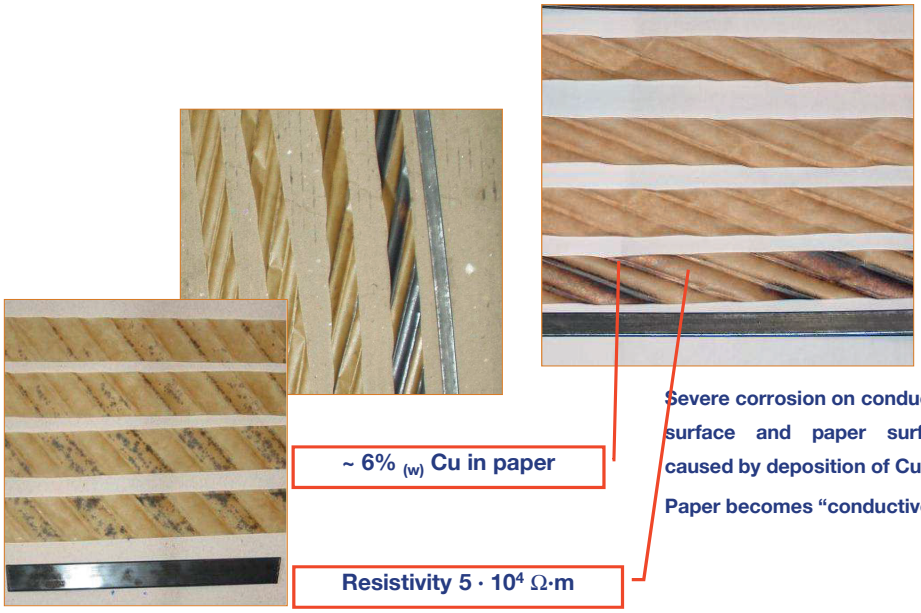
Paper and Copper Contamination



~ 6% $_{(w)}$ Cu in paper

Resistivity 5 · 10^4 Ω·m

Severe corrosion on conductor surface and paper surface caused by deposition of Cu_2S.

Paper becomes "conductive".

Paper Contamination

Copper sulfide (Cu_2S) is an electric semi-conductor

	Tan δ	Resistivity (Ωm)
Insulating windings paper, without visible copper sulfide contamination	0.003	5 · 10^{12}
Insulating windings paper, with low copper sulfide contamination	0.005	5 · 10^{10}
Insulating windings paper, with high copper sulfide contamination	> 1	5 · 10^4

Equipment faults by short-circuits between windings (arcing)

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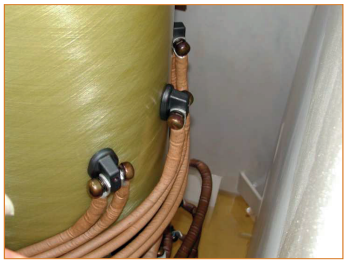
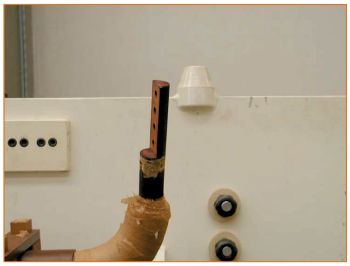
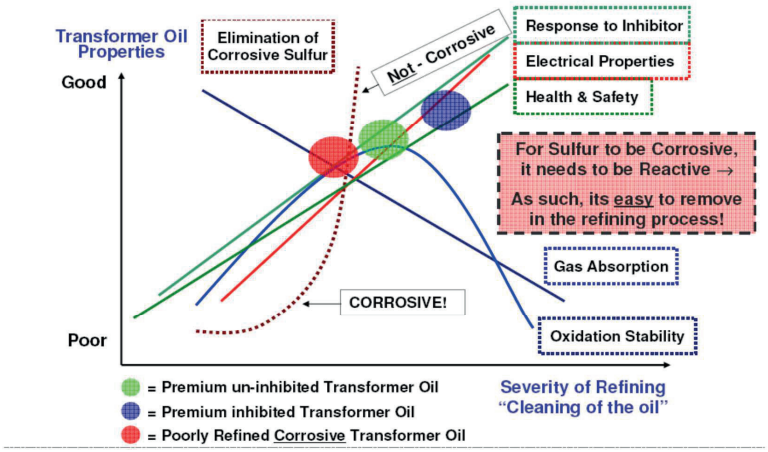
Inside the transformer



All the metallic surfaces of naked copper result covered by an adherent layer of black dust of Cu_2S



Sulfur overview



Herlenius Nils for
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June 2010
Slide No. 23

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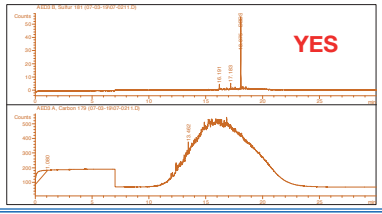
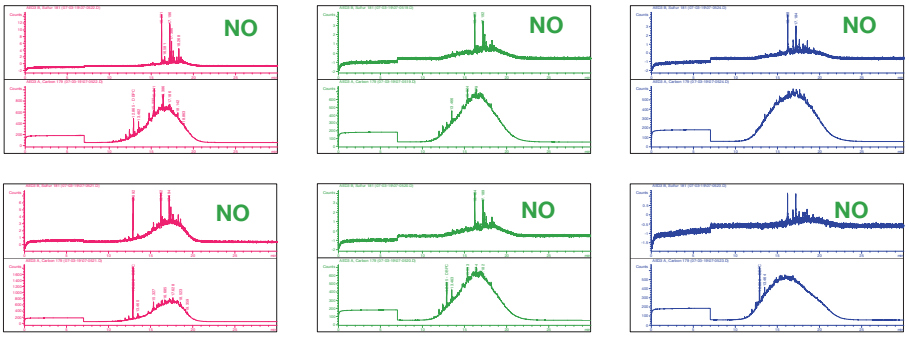
Best seller (producer 1) oil before DBDS Discovery

DBDS typically ~150 ppm

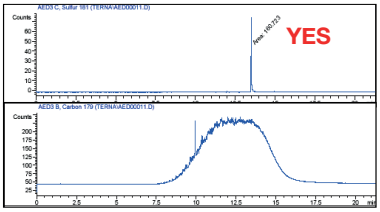


OILS ON MARKET AFTER DBDS DISCOVERY

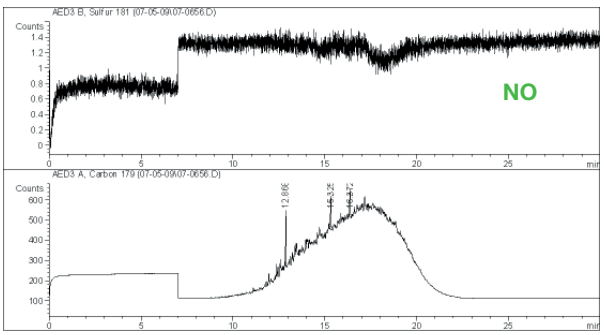


Best seller (producer 2) oil before DBDS Discovery

DBDS typically ~150 ppm



SAME OIL AFTER DBDS DISCOVERY



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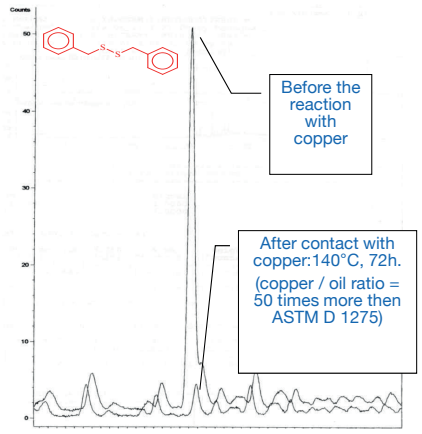
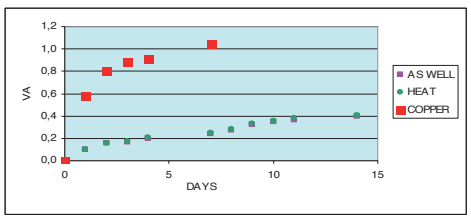
DBDS' behavior with copper



Oils containing DBDS were subjected to copper-to-oil reaction under the conditions prescribed in ASTM D 1275.

DBDS and oxidation stability

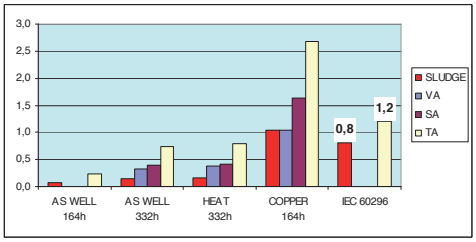
Oxidation stability tests were performed accordingly with IEC 61125 C, on unused oils containing DBDS. The same oil was tested again for oxidative stability.



AS WELL: oil with DBDS, untreated
HEAT: oil with DBDS pretreated 3 days at 140°C
COPPER: oil with DBDS pretreated 3 days at 140°C with copper

The oil meets IEC 60296 requirements as new and even after thermal stress.

After the reaction with copper (and consequent DBDS consumption) oxidation stability falls to unacceptable values.



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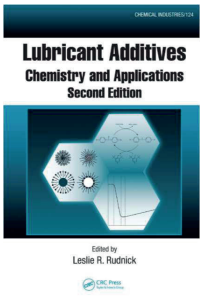
DBDS and oxidation stability

From "Lubricant Additives – Chemistry and Application" 2nd Edition 2008 – page 5 – Edited by Leslie R. Rudnik – CRC Press



The initial concepts of using antioxidants to inhibit oil oxidation date back to the 1800s. One of the earliest inventions described in the literature [1] is the heating of a mineral oil with elemental sulfur to produce a non-oxidizing oil. However, the major drawback to this approach is the high corrosivity of the sulfurized oil toward copper. Aliphatic sulfide with a combined antioxidant and corrosion inhibition characteristics was developed by sulfurizing sperm oil [2]. Additives with similar functionalities could also be obtained from sulfurizing terpenes and polybutene [3–5]. Paraffin wax has also been employed to prepare sulfur compounds [6–9]. Theoretical structures of several sulfur compounds are illustrated in Figure 1.1. Actual compounds can be chemically complex in nature. Aromatic sulfides represent another class of sulfur additives used as oxidation and corrosion inhibitors. Examples of simple sulfides are dibenzyl sulfide and dixylyldisulfide.

Unpredictability

Test	Factory	Laboratory	Substation	Results
PF% (Winding – 100 : 1000V)		X		Yes
PF% (Transformer)	X 10-70kV		X 1-10kV	No
Volumetric resistivity of paper (W-cm)		X		Yes
Power factor of paper (tang d)		X		Yes
FDS (Frequency domain spectroscopy)	X		X	No
SFRA (Sweep frequency Response Analyses)	X		X	No
RVM (Return voltage measurements)	X		X	No
Partial Discharges (476kV)	X			No

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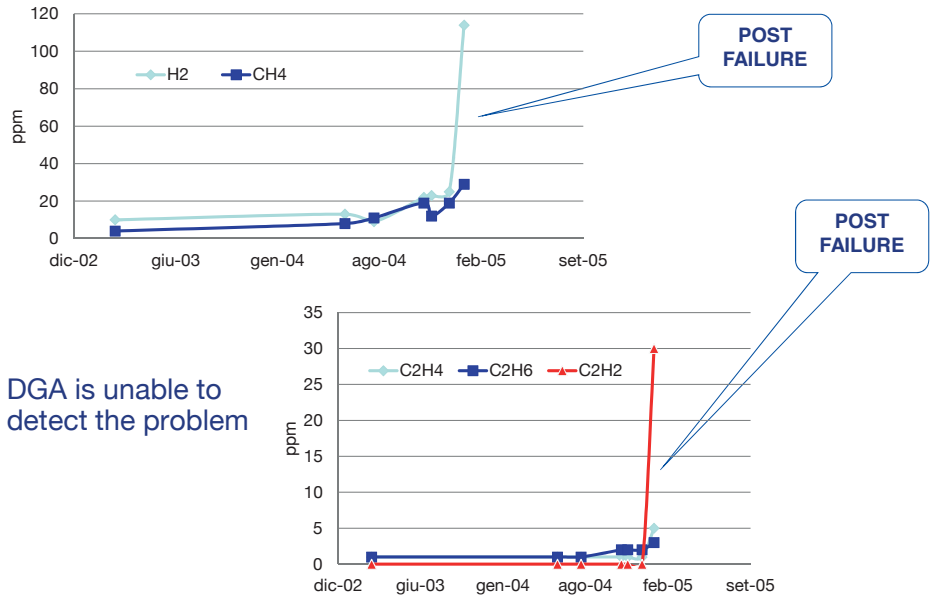
Unpredictability

Test	Laboratory	Substation	Results
DGA	X	X	No
Water	X	X	No
Chemical- Physical (NN, IFT, tan δ, BDV, etc.)	X		No
2-FAL and derivative	X		No
Corrosive sulfur (DIN 51353, silver, 100°C, 18 h)	X		No
Corrosive sulfur (ASTM D1275-A, copper, 140°C, 19 h)	X		No/ Yes
Corrosive sulfur (TERNA, copper, 140°C, 72 h)	X		No/ Yes
Corrosive sulfur (CIGRE CCD, copper and paper, 150°C, 72 h)	X		Yes
DBDS	X		Yes

Unpredictability



DGA is unable to detect the problem

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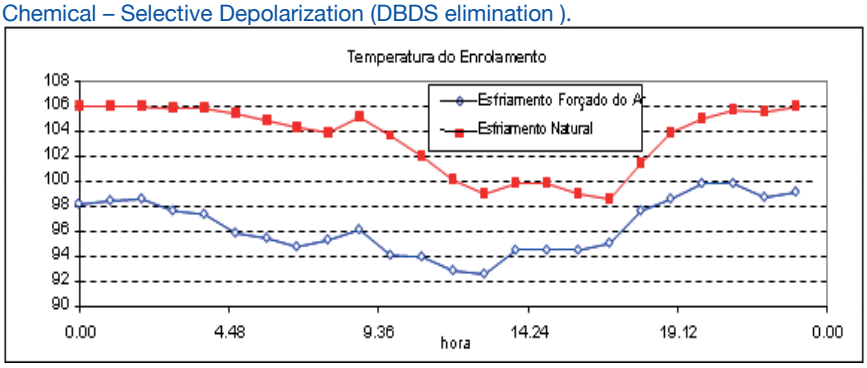
Mitigation Techniques

EQUIPMENT

- Winding replacement (high economic impact)
- Cooling improvement (only some cases).

OIL

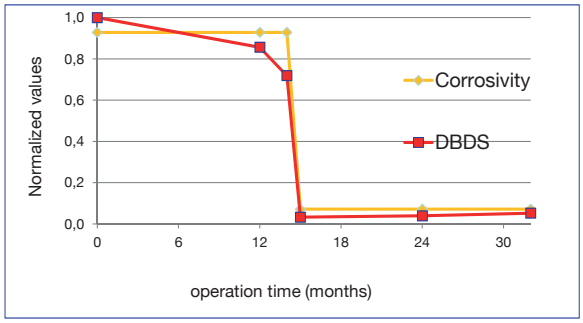
- Oil passivation with Irgamet 39 (worldwide used, but 38% of breakdown in Terna-Brazil experience)
- Oil retrofilling (no faults)
- Chemical – Selective Depolarization (DBDS elimination).



Retrofilling: Oil change

Operational history of a retro-filled shunt reactor 500 kV

Corrosiveness test code is based on ASTM D 1275-B, levels 1-12 correspond to tarnish levels 1a to 4c, where values higher than 9 are rated as corrosive



Time (months)	Action	Corrosiveness Test (ASTM D1275-B code)	DBDS (mg/Kg)
0	Start-up	11 (4b)	165
12		11 (4b)	131
14		11 (4b)	110
15	Oil change	1 (1a)	5
24		1 (1a)	6
32	Still in service	1 (1a)	8

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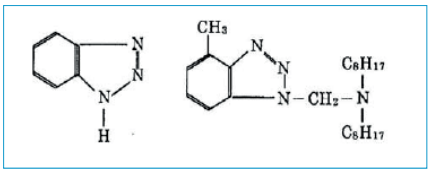
Passivation

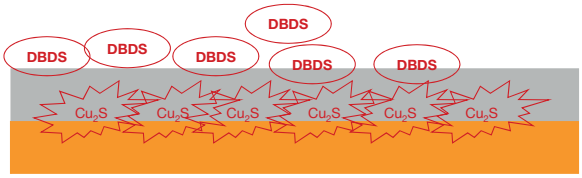
Source list of metal deactivators:

- **Irgamet® 30 Ciba Triazole derivative (liquid pure reagent)**
- **Irgamet® 39 Ciba Tolutriazole derivative (liquid pure reagent)**
- Irgamet ® 42 Ciba (water-soluble tolutriazole derivative)
- Irgamet® BTZ Ciba Benzotriazole
- Irgamet® TTZ Ciba Tolutrizole
- **Cobratec® TT100 Tolyltriazole (solid pure reagent)**
- **Nynas AB - Nypass (pre-blend of 10% passivator and a transformer oil base stock)**
- **Shell Diala Concentrate P (10% concentrate)**
- **DSI Sulphur Inhibitor – liquid concentrate mixture**
- Ethanox® 4705 Albemarle *N,N*-disalicylidene-1,2-diaminopropane
- Cuvan® 303 RT Vanderbilt *N,N*-bis(2-ehtylhexyl)-ar-methyl-1H-benzotriazole-1-methanamine
- Cuvan 484 RT Vanderbilt 2,5-Dimercapto-1,3,4-thiadiazole derivative
- Cuvan 826 RT Vanderbilt 2,5-Dimercapto-1,3,4-thiadiazole derivative
- NACAP® RT Vanderbilt Sodium 2-mercaptobenzothiazole, 50% active
- ROKON® RT Vanderbilt 2-Mercaptobenzothiazole
- Vanchem® NATD RT Vanderbilt Disodium, 2,5-dimercaptothiadiazole, 30% active
- Vanlube 601 RT Vanderbilt Heterocyclic sulfur–nitrogen compound
- Vanlube 601E RT Vanderbilt Heterocyclic sulfur
- Vanlube 704 RT Vanderbilt Proprietary blend



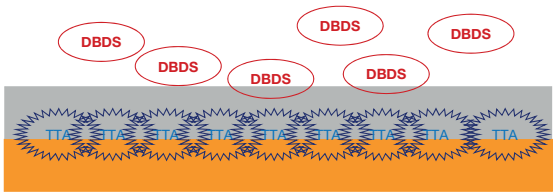
CAS No.: 94270-86-7, Tolutriazole Derivative
Molecular Formula: N,N-bis(2-ethylhexyl)-ar-methyl-1H-benzotriazole-1-methanamine

Passivation



TTA and derivatives react to copper surface

Manufacturers recommendation usage is 100 mg/Kg

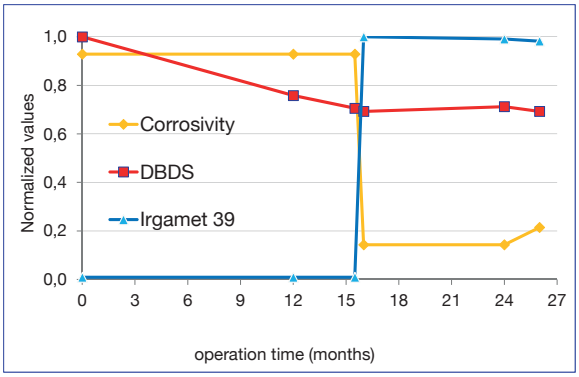


Corrosive Sulfur in Transformer Insulating Mineral Oil: What is it and how to prevent the Adverse Effect

Passivation

Operational history of a passivated 500 kV shunt reactor, failed 10 months after passivation

Corrosiveness test code is based on ASTM D 1275-B, levels 1-12 correspond to tarnish levels 1a to 4c, where values higher than 9 are rated as corrosive

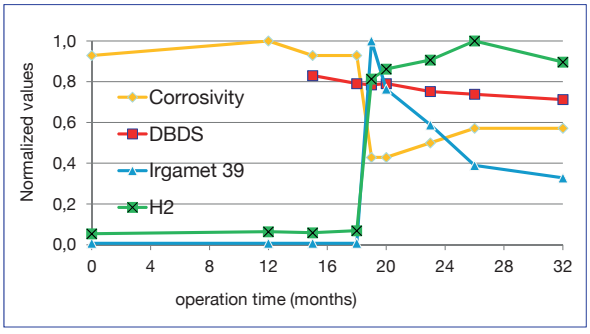


Time (months)	Action	Corrosiveness test (ASTM D1275-B code)	DBDS (mg/Kg)	Irgamet 39 (mg/Kg)
0	Start-up	11 (4b)	153	< 1
12		11 (4b)	116	< 1
15		11 (4b)	108	< 1
16	Passivation	2 (1b)	106	112
24		2 (1b)	109	111
26	Failure	3 (2a)	106	110

Passivation & Side Effects: Stray gassing

Operational history of a passivated 380 kV power transformer, with stray gassing generation

Corrosiveness test code is based on ASTM D 1275-B, levels 1-12 correspond to tarnish levels 1a to 4c, where values higher than 9 are rated as corrosive



Time (months)	Action	Corrosivity (ASTM D1275-B)	DBDS (mg/Kg)	Irgamet 39 (mg/Kg)	H_2 (µ//l)
0	Start-up	11 (4b)	unknown	< 1	11
12		12 (4c)	unknown	< 1	13
15		11 (4b)	127	< 1	12
18		11 (4b)	121	< 1	14
19	Passivation	5 (2c)	120	131	165
20		5 (2c)	121	100	175
23		6 (2d)	115	77	184
26		7 (2e)	113	51	203
32	Still in service	7 (2e)	109	43	182

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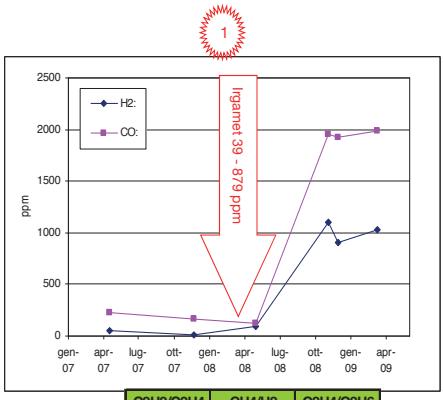
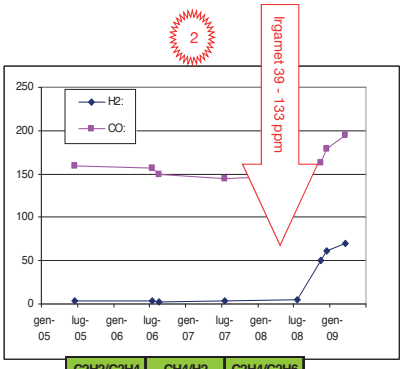
Passivation & Side Effects: Stray gassing

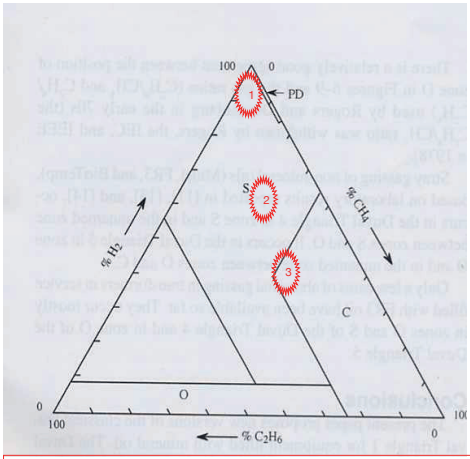


C2H2/C2H4	CH4/H2	C2H4/C2H6
0,00	0,03	0,19
IEC 60599		
-	< 0,1	< 0,2
PARTIAL DISCHARGES		



C2H2/C2H4	CH4/H2	C2H4/C2H6
0,00	0,10	0,02
IEC 60599		
-	< 0,1	< 0,2
PARTIAL DISCHARGES		

Passivation & Side Effects: Stray gassing



Modified version of Duval Triangle, from IEEE Electrical Insulation Magazine volume 24-6
zone S: stray gassing of mineral oil
zone C: hot spots with carbonization of paper (>300°C)
zone O: overheating
zone PD: corona partial discharges

DGA misinterpretation may be partially overcame using the modified version of Duval Triangle

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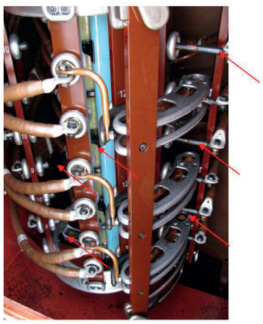
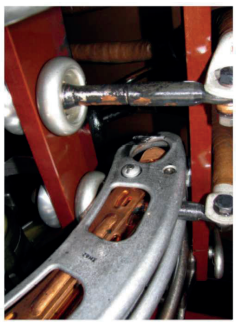
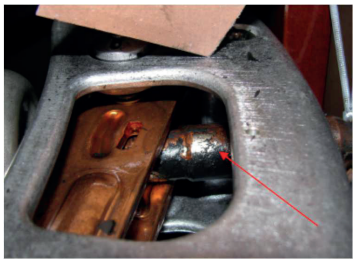
Passivation: silver corrosion



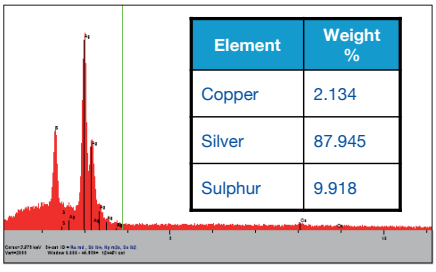




230/130 kV 150 MVA Transmission TR:

- Age: 5 years
- Filled in 2005 with Italian oil, later discovered as corrosive (DBDS: 150 ppm)
- Passivated two years later in 2007
- No Irgamet 39 depletion over the years
- Failed in February 2010
- Inspected in May 2010, by manhole

Passivation: silver corrosion



Element	Weight %
Copper	2.134
Silver	87.945
Sulphur	9.918

SEM/EDX

Mechanism:

- Pre-selector OLTC's copper parts are not corroded
- Pre-selector OLTC's silver parts are completely corroded
- Build-up of Ag_2S on the conductor surface until the film becomes mechanically unstable
- Transportation of Ag_2S particles

- Breakdown at power frequency and rated voltage stress?

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Passivation

Most widely mitigation action used
Found to be effective in the large majority of cases
Some cases of failure, where critical conditions for instability did exist. Some evidences come from:

- Brazil, 9 shunt reactors failed in a range of 1 ÷ 22 months later
- Brazil, 1 GSU (hydraulic) failed after passivation
- USA, 1 GSU (thermal) failed after 1 year from passivation

	Corrosiveness persistence	Irgamet 39 consumption	Stray gassing			
			H_2	CO	CO_2	C_xH_y
%	8	39	33	16	16	4

Long time survey (complied over 5 years) on more than 1000 reactors & transformers

Selective Depolarization

Industrial application:
- more than 250 transformers
- several kTons of oil treated

Principles of the process:
- The process is performed on-site
- The process is performed in closed-circuit, without emptying the unit even partially
- The process can be operated on loaded transformers, up to 500 kV of rated voltage

- The oil is firstly forced through a solid chemical reagent that convert DBDS and other corrosive compounds in a more polar by-product
- A second step of solid reagents blocks the corrosive compounds previously converted
- The oil is submitted to degassing and de-humidification before reverting back in the transformer

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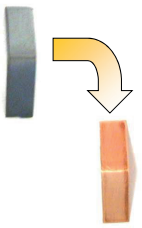
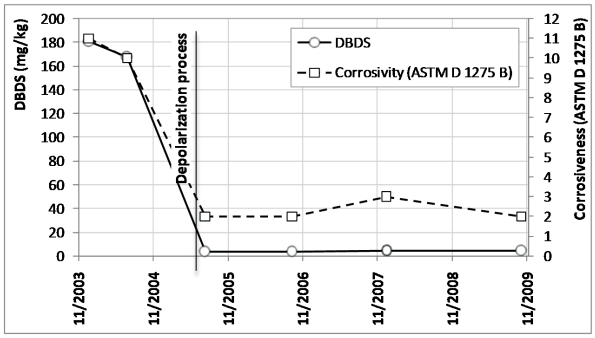
Corrosive Sulfur in Transformer Insulating Mineral Oil: What is it and how to prevent the Adverse Effect

Selective Depolarization

Real case of Selective Depolarization – survey of oil's parameters after the treatment

Parameter	Units	Value
Power	MVA	15
Rated voltage	kV	15
Oil type	-	Nynas Nytrafo 11
Year of installation	-	2000
Cooling mode	-	ONAF
Segregation	-	Breathing





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Comparison

	PASSIVATION	OIL CHANGE	DEPOLARIZATION
SIMPLICITY	☺	☺ / ☹	☹
TIME CONSUMING	☺	☺ / ☹	☹
ON LOAD	Not applicable	Not applicable	☺
EFFICIENCY	☹	☺ / ☹	☺
OIL'S PROPERTIES IMPROVEMENT	☹	☺	☺
LONG TERM PERFORMANCE	☹	☺	☺
ENVIRONMENTAL	Unknown	☹	☺
COST	☺	☺ / ☹	☺ / ☹

Corrosive Sulfur in Transformer Insulating Mineral Oil: What is it and how to prevent the Adverse Effect

Conclusion

DBDS is like the rust: it never sleeps!

Thanks for your attention