“DBDS & CORROSION FREE” Programme: Diagnosis and Countermeasures

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President and Founder of Sea Marconi Technologies, Turin (Italy); Ass. Secretary of IEC TC10
Coauthors, Maina Riccardo, Tumetti Michela and Roggero Carlo
Sea Marconi Technologies

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Sea Marconi introduction 1/3

Headquarter:
Collegno (Turin, Italy)

Homécourt (Region of Lorena, France)

Sea Marconi introduction 2/3

- **Foundation**: 1968, by Vander Tumiatti in Turin Italy
- **Mission**: Protection of company assets and environmental resources
- **Activities**: Research, Technologies, Services and Products for Energy & Environment
- **Clients**: > 3,000 users in the energy, industry and service sectors in Europe, South America and others countries
- **Human resources**: 101 employees, engineer, doctors (chemistry, mechanics, economics, ICT, etc.) and qualified technicians
- **Diagnostics**: EN ISO 17025, Databases, hi-tech instruments
- **Decontamination**: on site Mobile Units (DMU) different sizes
- **Quality**: ISO 9001-2000, Niszert (Sea Marconi Tecnologies)
- **Patents**: EEC, USA, others countries patented processes
- **R & D**: Qualified by Italian Ministry of University and Scientific Research
- **European Project**: HALOCLEAN APPLICATION; contract number - G1RD-CT-2002-03014 (Principal Main Contractor)
- **Experts**: members in WGs (IEC, CEN, CIGRE)
Sea Marconi - Laboratory 3/3

Advanced analysis methods.
Quality certification:
ISO 9001/2001; ISO 17025-2000

Our laboratory analysis is among the best in the world:
- for the range of tests performed
- for the technologically advanced instrumentation
- for the methodologies used

SINAL-ILAC CERTIFICATION

Accredited tests:
- PCB, PCT, PCBT, according to IEC 61619:1997-04; EN 12766-3:2004

Sea Marconi - Methods 1/4

Integrated methods for Diagnostic and Treatments similar to “Human Blood”...

...contacting internal organs for which diagnostic Tests and dialysis therapies” is metaphorically used
Rapresentative Sampling for Diagnostic Tests

Transformer oil

"Human Blood"

Dedicated laboratory analyses for diagnostics

Sea Marconi lab

"Typical Hospital lab"
Sea Marconi - Kits

**Inspection and Sampling Kit Deos TR®**

- Single-use gloves
- Single use flasks (125 ml)
- Glass syringe (50 ml)
- Label
- Three way valve
- Plug (¼”)
- n. 2 silicon pipes
- Plastic bag for delivery
- Sampling datasheet

**Kit DeosTR® and DeosTR+® do not include:**
- paper or tissues for cleaning,
- vessels for waste oil and liquids,
- fitting plugs for connection.

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Sea Marconi - Methods 4/4

**Integrated, in continuous and on-load fluid treatments**

- **DMU by Sea Marconi for Integrated treatments of oil**
- **“Human Blood Dialysis”**
Typical DMU configuration

Integrated treatments: Decontamination, Depolarization, Detoxification

Detoxification of PCBs/PCTs/PCBTs, POPs, compounds etc.

Elimination of dissolved organo-metallic contaminants

Elimination of sulfur corrosive contaminants, DBDS

Recovery of chemical properties of the oil (acidity, delta tg, colour)

Recovery of dielectric properties

Multifunctional Technologies and Process

<table>
<thead>
<tr>
<th>Main function</th>
<th>Physical decontamination</th>
<th>CHEDCOS depolarisation</th>
<th>CDP PROCESS® dehalogenation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Recovery of dielectric properties</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Recovery of the chemical properties of the oil</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Elimination of sulfur corrosive contaminants, DBDS</td>
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<tr>
<td>Elimination of dissolved organo-metallic contaminants</td>
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<tr>
<td>Detoxification of PCBs/PCTs/PCBTs, POPs, compounds etc.</td>
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<td></td>
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</table>
Sea Marconi - PCBs Free Solutions

CDP Process®

Sea Marconi – CDP Process®

After CDP Process®, reclassification “NO PCB” of Transformer and Oil

Before dehalogenation

After dehalogenation
Sea Marconi - Corrosive Sulfur Solutions

Chedcos

Sea Marconi - Chedcos®

Selective Depolarisation and DBDS elimination

Effect of the CHEDCOS® selective depolarisation process: chemical decomposition of corrosive compounds “DBDS”
Transformer in oil

Nikola Tesla inventor

(10/071856 – 7/01/1943)

- “Electrical Transformer” Patent n. 493,138, November 2, 1887
- “Electrical Transformer or induction device”, Patent n. 433,702, August 15, 1890
- “Method of Insulating Electric Conductors” Patent n. 655,838, August 14, 1900

“my invention any kind of fluid capable of meeting the requirements (75…) as oil, may be used (130…)”

Transformer applications

Transformer and insulating liquids in generation, transmission and distribution for electrical networks
Transformer Fleet

FLEET & FAMILY
- Type
- Power (MVA)
- Voltage (KV)
- Age (year)
- Fluid
- Manufacturers
- Value (€)
- Consuming life

Insulating Oils

NATURAL & ENERGY RESOURCE
- 90% FUELS
- 3% BITUMENS
- 1% BASE OIL
- 0.01% TRANSFER OIL (ex.)

REFINING
- ADDITIVES
- EFFECTS ON HUMAN HEALTH & ENVIRONMENT
- WASTES & RECOVERY
- LCA (Life-Cycle Analysis)

<table>
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<tr>
<th>COUNTRY</th>
<th>Oil Volume (ton)</th>
<th>Total Volume (ton)</th>
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</thead>
<tbody>
<tr>
<td>Australia</td>
<td>192.5</td>
<td>548</td>
</tr>
<tr>
<td>Canada</td>
<td>483.5</td>
<td>800</td>
</tr>
<tr>
<td>France</td>
<td>372.8</td>
<td>820</td>
</tr>
<tr>
<td>Germany</td>
<td>844.3</td>
<td>765</td>
</tr>
<tr>
<td>Italy</td>
<td>784.8</td>
<td>525</td>
</tr>
<tr>
<td>Japan</td>
<td>554.7</td>
<td>1419</td>
</tr>
<tr>
<td>United Kingdom</td>
<td>137.5</td>
<td>475</td>
</tr>
<tr>
<td>USA</td>
<td>792</td>
<td>8600</td>
</tr>
</tbody>
</table>

Notes:
- Oil volume based on 1,000 L/d Oil consumption
- Total volume includes transport and storage
- Comparative figure for ten nCIE LCIE (U.S. Oil)

PCAs/PAHs
Oil & Generation Transformers - Asset value

- > 10,000 million litres of insulating oils
- Typical replace value is more than 1 € / litre
- Insulating Oil represent ~ 6% value of transformer
- Insulating Oil represent ~ 25% weight of transformer

OECD - Total Asset Value: Generation Power Transformer

> 150,000 million € - Euro

Typical Faults

- DBDS & Corrosive Sulfur
- Electrical Fault-Arching
- Paper degradation and sludging
- Thermal Fault-Hot spot > 700 °C

Copper in oil (mg/kg) vs Service Period (Years)

No-Sulfur Corrosion
Focus

Protection of Resources Assets & Environment

- Failure
- Explosion
- Fire

- Black-Out

- Infancy
- Occasional
- Old age

Focus

Prevention and/or mitigation of...

...Black-Out impact (3 to 36 hours)

- No energy for:
  - > 55 million people (September 2003 in the whole of Italy)
  - > 15 million people (August 1994 Southern Italy only)
  - Industries (petrochemical, steel-mills, mechanical)
  - Services (hospitals, schools, research, utilities)
  - Defence

- Damages
  - Direct: Assets & Personal
  - Indirect: Production
  - Environment: soil, water, air
IEC Standards

IEC 60296 and IEC 60422

IEC Standards

NORME INTERNATIONALE
INTERNATIONAL STANDARD

IEC IEC

60296

3.3 additive suitable chemical substance which is deliberately added to a mineral insulating oil in order to improve certain characteristics

NOTE: A large number of antioxidant additives are available. For this standard, limits are limited to those identified in IEC 60906.
6.9 Sulfur content

Different organo-sulfur compounds are present in transformer oils, dependent on the crude oil origin and the degree and type of refining. Refining treats sulfur and aromatic hydrocarbons. As some sulfur compounds have an affinity to metals, they may act as copper passivators or they may promote corrosion.

Sulfur content should be measured following BS 2000 Part 373 or ISO 14596.

6.10 Corrosive sulfur

Some sulfur compounds, e.g. mercaptans, are very corrosive to metal surfaces, i.e. steel, copper and silver (switchgear contacts) and shall not be present in new oil. Corrosive sulfur should be measured following DIN 61353.
The recommendations for concentration limit for Corrosive Sulfur compounds in oils (CIGRE A2.32 figure 9, pag. 31):

- "<10 mg/kg for DBDS (after 90 days);
- < 5 mg(S)/Kg total difulphides + mercaptans content in oil." Total Corrosive Sulfur compounds (after 90 days)
Case history

Case history of Total Sulfur in oil (considerable reduction since 1990)

DISTRIBUTION TRANSFORMERS (<72,5kV ; <10MVA): tot. no. 4970

Total Sulfur

Case history of dissolved Hydrogen in oil (considerable increment since 1990)

DISTRIBUTION TRANSFORMERS (<72,5kV ; <10MVA): tot. no. 5024
Case history

**Case history of Dissolved Copper in oil**
(considerable increment since 1990)

**DISTRIBUTION TRANSFORMERS (<72,5kV ; <10MVA): tot. no. 4970**

**Dissolved copper**

![Graph showing the trend of ratio \(\text{lt}/\text{KVA} (\text{Oil})\) over years.](image)

**Population:** 50,000 transfo (Data Base Sea Marconi)

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**Case history**

**Case history**

**Trend of ratio \(\text{lt}/\text{KVA} (\text{Oil})\)**

**Population:** 50,000 transfo (Data Base Sea Marconi)
Corrosion phenomena

Materials present in a transformer:
Iron, copper and other (minor) metals
Oil/insulating liquids
Cellulose or other solid insulation
Wood and pressboards
Rubber, glues, polymers, etc.

Possible chemical interactions between different materials:

Acid corrosion (oil to copper, oil to iron)
Formation of complexes (oil to copper, oil to iron)
Catalysis of redox reactions (acids, water, additives)
Oxidation (oxygen, peroxides to oil/cellulose)
Dissolution of soluble compounds (oil to rubber, oil to polymers)

Corrosion phenomena

Contaminants resulting from corrosion:
Dissolved copper (and other metals)
Suspension copper (and other metals)
Copper complexes
Insoluble copper salts (copper sulfides, copper oxides)

Classification of corrosion phenomena:
Related to copper sulfide formation (Corrosive Sulfur)
copper sulfide growth on naked conductors
copper sulfide growth on solid insulation

Related to copper formation (NO-Sulfur Corrosion)
dissolved/suspended copper in oil
copper deposition/adsorption on solid insulation
Case history of failures
Due to Corrosive Sulfur on a 500 KV line – Brazil

### TSN

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<tr>
<th>Component</th>
<th>Quantity</th>
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<td>Lines</td>
<td>1181 km</td>
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<tr>
<td>Substations</td>
<td>6</td>
</tr>
<tr>
<td>Total reactors</td>
<td>40</td>
</tr>
<tr>
<td>Reactors with Corrosive Sulfur</td>
<td>37 (92.5%)</td>
</tr>
<tr>
<td>Total failed reactors</td>
<td>15 (37.5%)</td>
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</table>

### Novatrans

<table>
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<tr>
<th>Component</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lines</td>
<td>1278 km</td>
</tr>
<tr>
<td>Substations</td>
<td>6</td>
</tr>
<tr>
<td>Total reactors</td>
<td>36</td>
</tr>
<tr>
<td>Reactors with Corrosive Sulfur</td>
<td>13 (36.11%)</td>
</tr>
<tr>
<td>Total failed reactors</td>
<td>-</td>
</tr>
</tbody>
</table>

Corrosive Sulfur: related failures

- Failures related to Corrosive Sulfur encountered in last years

- Failure
- Presence of deposits of Cu$_2$S
Corrosive Sulfur: related failures

Copper sulfide: main cause of fault or co-factor?

Heavy formation of copper sulfide on naked copper, failure due to a discharge between LV conductors and the grounded tank.

Heavy formation of copper sulfide on inner solid insulation, failure due to a turn-to-turn discharge.
Corrosive Sulfur: related failures

Copper sulfide: main cause of fault or co-factor?

Evidence of general overheating in the faulty winding. High temperature was the main factor of the fault.

Copper sulfide found on conductors.

Copper sulfide found on inner layer of cellulose. [Cu] > 10% by weight
DBDS Discovery

July 2005, DBDS in oil - First identification

Sea Marconi’s laboratory

IFED (Integrated Fingerprinting & Elemental Diagnostics) techniques, using HRGC-AED&MS

DBDS confirmation

DBDS (DiBenzylDiSulfide) in Oil

“Sulfur compound, very corrosive to metal surface (i.e. steel, copper and silver) at normal operating temperatures”
**DBDS confirmation**

**DBDS “Antioxidant additive” in oil**

R. Naima, F. Scatiglio, S. Kapila, N. Tumiatti, V. Tumiatti


3037. Dibenzyldisulfide. [150-60-7]

Bis(phenylmethyl)-disulfide; benzyl disulfide; α-(benzylthio)toluene; di(phenylmethyl)disulfide.

C₁₄H₁₂S₂, mol wt 240.20, C 64.24%, H 5.73%, S 26.03%. C₁₄H₁₂(SCH₂CH₃)₂. Prepd by the reaction of benzyl chloride with sodium disulfide or polysulfide: Blanesma, Rec. Trav. Chim. 20, 137 (1901); Koran, Condall, US 2113092 (1938); Wojcik, US 2185007 (1939).

Melting point: 71-72° C. Another modification mp 65-70°C. Decomposes at > 770°C. Practically insoluble in water. Soluble in ether, benzene, hot methanol, hot ethanol.

Use: Antioxidant in rubber compounding, stabilizer for petr fractions, additive to silicone oils. The solubility in oils is increased by the presence of benzyl alcohol.

**DBDS confirmation**

Example of IFED of “Sulfur profiles” in oil
DBDS confirmation

- Oil
- DBDS
- Cu
- Temperature > 100 °C

\[ \text{CU}_2\text{S} \]

“Winding Hot-spot temperature in °C” Ref. IEC 60076-7 Ed. 1

“Power Transformer – Part. 7: Loading guide for oil – immersed power transformers”

DBDS & Occurrence

Occurrence of DBDS in corrosive oils

Considering as 10 mg/kg of DBDS the threshold to make an oil corrosive, 93.4% of oils in this population takes its corrosiveness from DBDS
A typical mechanism for conversion of DBDS in copper sulfide and byproducts

\[
\text{DBDS} + \text{Cu} \xrightarrow{T (>100 \degree C)} \text{Cu}_2\text{S}/\text{CuS}
\]

Cuprous/cupric sulphide

Dibenzyl sulphide
Benzyl mercaptan
Toluene
Stilbene

DBDS & Corrosive Sulfur: related failures

Copper sulfide: main cause of fault or co-factor?

Copper sulfide found on inner layer of cellulose.

\[[\text{Cu}] > 4\% \text{ by weight}\]

Symptom: decay of DBDS during the service
The Qualitative Test Method (IEC 62535 Ed.1 2008-10) can provide results "False Positive" (up to 80% of “Potentially Corrosive”), in case of used and/or degraded oils and “False Negative” (100% of “No-Potentially Corrosive), in case of oils with DBDS (typical range 150-250 mg/Kg) but with passivator additives, masking the visual effects during the 72 hours of the test.

In case of doubts in the interpretation of inspection result of the paper, the composition of the precipitate must be analyzed with other methods as, for example, the SEM-EDX. This is a complex instrumentation, very expensive, not easy available, providing, in any case, qualitative results only.
### Total Corrosive Sulfur - SM-TCS

**The new Quantitative SM-TCS Test Method (Sea Marconi - Total Corrosive Sulfur, patent applied for)**

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>GC – ECD DBDS mg/kg</th>
<th>GC-MS DBDS mg/kg</th>
<th>GC-AED DBDS mg/kg</th>
<th>SM-TCS DBDS eq. mg/Kg</th>
<th>Ave.</th>
</tr>
</thead>
<tbody>
<tr>
<td>37 – A</td>
<td>129</td>
<td>116</td>
<td>126</td>
<td>141</td>
<td>144</td>
</tr>
<tr>
<td>37 – B</td>
<td>129</td>
<td>106</td>
<td>133</td>
<td>142</td>
<td>103</td>
</tr>
<tr>
<td>37 – C</td>
<td>71</td>
<td>76</td>
<td>62</td>
<td>83</td>
<td>143</td>
</tr>
<tr>
<td>37 – D</td>
<td>4.00</td>
<td>&lt;2.0</td>
<td>&lt;2.0</td>
<td>&lt;10.0</td>
<td>&lt;10.0</td>
</tr>
<tr>
<td>37 – F</td>
<td>&lt;2.0</td>
<td>3.00</td>
<td>N.R</td>
<td>&lt;10.0</td>
<td>&lt;10.0</td>
</tr>
<tr>
<td>37 – G</td>
<td>24</td>
<td>56</td>
<td>N.R</td>
<td>31</td>
<td>80</td>
</tr>
<tr>
<td>37 – H</td>
<td>69</td>
<td>101</td>
<td>145</td>
<td>94</td>
<td>118</td>
</tr>
</tbody>
</table>

Results of the IEC TC 10 WG37 Round Robin Test n.1

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**Sea Marconi – Total Corrosive Sulfur** test methods (Patent pending 2008) is able to offer a very effective and reliable solution for the determination of total corrosive sulfur, despite the presence of passivating additives.

**SM-TCS strong points:**

- Total corrosive sulfur quantification (3mg/Kg)
- Disclosure of passivating effects inside the oil
- Resolution of any interpretative doubt
- Significantly reduced time for final response (16 hours)
- No lab facilities required
**Total Corrosive Sulfur - SM-TCS**

- Washing solvents
- Deionized water
- Pipettes
- Sealed vials with copper powder and magnetic bar (Argon atmosphere)
- Needles for syringes
- Silicon tube
- Filters (P.A. 0.45 μm)
- Gloves
- Litmus
- Aluminium caps
- Bottles for final solutions
- Plastic syringes
- Pipettes
- Sealed vials with copper powder and magnetic bar (Argon atmosphere)
- Reagents

**Sample preparation**

- Reaction between oil & copper - oxidation

- Sulphates dissolution in water

- Sulphates quantification
The new **SM-IFED** Test Method (Sea Marconi - Integrated Fingerprint & Elemental Diagnostic – patent pending) solves all types of analytical uncertainty and interpretation doubts with results referred to a univocal comparison (Qualitative and Quantitative) of the “Data Base Profiles”
Oil Fingerprinting Profile – SM – IFED (3/6)

SM-IFED Results: “Naphthenic Base Oil with DBDS”-NYNAS NYTRO 10 GBN

IFED with GC-AED fingerprinting

DBDS

Distillation profile

Oil Fingerprinting Profile – SM – IFED (4/6)

SM-IFED Results: “Naphthenic Base Oil with DBPC & NO-DBDS”-NYNAS 10 XN-2005

IFED with GC-AED fingerprinting
These two oils were proposed to one customer by two different oil companies (one Italian, one German), with different brands and different names.

Oils have the same carbon and sulfur fingerprint.

They are the same oil.

SM-IFED Results: “Naphthenic Base Oil with DBDS”- Oils Producer A & B

SM-IFED Results: “Naphthenic Base Oil with Medium Total Sulfur & NO-DBDS”-Oil Producer X
“DBDS & Corrosion Free Program” - Key Factors

1. Age: from 1988;
2. Type of mineral insulating oils: naphthenic base uninhibited oil without antioxidant additives (DBPC); other type of oils blended with naphthenic oil contaminated by Corrosive Sulfur;
3. Type of equipment: GSU; Shunt Reactors, HVDC transformers; industry transformers (rectifier, furnace, etc); highly loaded transmission transformers and secondly on other power or strategic transformers; OLTC; Bushings; Instrument transformers;
4. Top-up or oil change: > 5-10 %;
5. High load; High temperature;
6. Thermal fault: DGA (type: T1,T2,T3); trends in oxygen content symptoms of overheating;
7. Total Corrosive Sulfur Compounds (> 5 mg/kg) and or DBDS (> 10 mg/Kg) for unused oil. Typical concentration of DBDS: range 150-250 mg/Kg) and trends symptoms of formation of copper sulfide;
8. No spare part unit available;
9. Sister unit had suspect failure in the last 20 years;
10. Voltage level >220 KV.

ABC INVENTORY of strategic units by families

Identify one strategic unit representing each family of the same fleet of equipment, possibly by the same manufacturer, through an analysis of the following factors of evaluation:

**A**-Age : < 5 years; 5-10 years; >10-20 years;
**B**-Type: GSU; Shunt reactors, HVDC transformers; industry transformers (rectifier, furnace, etc.); highly loaded transmission transformers and secondly on other power or strategic transformers;
**C**-Power (MVA): <10; 10-50; 51-100; >100
1. **A** - Evaluación de la “Historia familiar anamnesis”  
   **B** - “Equipo”  
   **C** - “Síntomas”
2. Examen externo (“Síntomas”) del equipo; 
3. Muestreo representativo de la corriente aislante de cada equipo (**A; B; C**); 
4. Análisis (“Síntomas”) por un laboratorio credenciado y experto ISO 9001

4.1. Corrosión Total del Sulfuro-SM-TCS;  
4.2. Perfil de Huellas de Aceite - SM-IFED con GC/AED;  
4.3. Sulfuro Potencialmente Corrosivo (SCCD) – IEC 62535;  
4.4. DiBencilo DiSulfido (DBDS) con GC/MS & AED o ECD-IEC TC 10 WG 37;  
4.5. Aditivos Passivador de Metal - Ciba Irgamet 39;  
4.6. Aditivos Passivador de Metal - Benzotriazol-BTA;  
4.7. Contenido de aditivos inhibidores - DBPC-IEC 60666;  
4.8. Contenido de Sulfuro Total con ICP;  
4.9. Bisbencilo (BiBZ) con GC/MS;  
4.10. Bisbencilo (BiBZ) con GC/MS;  
4.11. Contenido de aditivos metálicos (Cobre, Hierro, Zinc, Selenio, Silicio, Plata, Alúmina) con ICP;  
4.12. Prueba de Depósito de Cobre (en el papel CCD) con ICP;  
4.13. Contenido de Partículas (cuentas y tamaños) - IEC 60970;  
4.14. Disolventes de Gases (DGA) - IEC 60657 y IEC 60599;  
4.15.2. Furfurilo y compuestos relacionados (Furans)-IEC 61198;  
4.16. Contenido de Agua - IEC 60814;  
4.17. Número de Acidez Total (TAN) - IEC 62021;  
4.18. Factor de Dispersión Dielectrónica (DDF) - IEC 60247;  
4.19. Resistividad - IEC 60247;  
4.20. Aspecto y Color — ASTM D 1500;
5. Trend Analysis, Evolution Rate, Data Base matching;
6. Diagnosis with interpretation of the Facts (Anamnesis, Signs, Symptoms) and Test Reports
7. Countermeasures for each unit representing a family

Post mortem and/or post failures diagnosis

It becomes necessary to perform post mortem and/or post failure inspections for diagnostic protocol to prevent and/or mitigate critical factors on fleets of equipment in operation belonging to the same family.
A typical example on a GSU Transformer of an Integrated Gasification Combined Cycle (IGCC).
Case History: Equipment Type- GSU; Power 192 MVA; Voltage max 400 KV; Year-1998; Manufacture A; Oil Type - Naphthenic Base Oil with DBDS; Oil Producer A; DBDS 110 mg/kg; Year of Failure 2006.
A case of failure related to Corrosive Sulfur (1 di 7)

- Inspection and Analysis on internal HV windings

3-4/October/2006
OPENING OF THE TRANSFORMER

From the outside, the failure appears due to electric discharge at the 17° turn, radial sector 8 (numbering the sectors from 1 through 24 in counterclockwise direction, no. 1 is in correspondence with the HV contact).

Pressboard damaged by the failure

Failure area, extended about 30x30 cm
Post mortem and/or post failures diagnosis

A case of failure related to Corrosive Sulfur (3 di 7)

- Inspection and Analisys on internal HV windings

Sinusoidal deformations of the windings, sector opposite to the failure

Internal view of the HV winding, failure zone

Post mortem and/or post failures diagnosis

A case of failure related to Corrosive Sulfur (4 di 7)

- Inspection and Analisys on internal HV windings

MAPPING OF THE COPPER CONTAMINATION
A case of failure related to Corrosive Sulfur (5 di 7)

- Inspection and Analysis on internal HV windings

VISUAL MAPPING OF THE COPPER SULFIDE DEPOSITS

A case of failure related to Corrosive Sulfur (6 di 7)

- Inspection and Analysis on internal HV windings

MAPPING OF THE THERMAL DEGRADATION
A case of failure related to Corrosive Sulfur (7 di 7)

- Inspection and Analysis on internal HV windings

COLLECTION OF PAPERS FROM THE WINDING
- Internal conductors of the winding heavily contaminated by copper sulfide. The strong corrosiveness of the oil (corrosiveness code: 4c, by repeated analyses according to ASTM D 1275 A ext. 48h) caused the deposition of elevated amounts of copper sulfide on the paper components.

Solutions

"DBDS & Corrosion Free Program"

The "DBDS & Corrosion Free Program" has the purpose of preventing/mitigating the risks associated with Corrosion Phenomena for the best protection of the fleet of equipment and oils (unused and used) through diagnostic, inventory, management and integrated treatments of insulating liquids for Life Cycle Management of transformer.
Supply technical specifications and standard references:
A. Additional requisites required by the purchaser and certified by the supplier for each lot of mineral insulating oil provided and equipment:
   - compliance with standard IEC 60296 Ed 3 2003-11
   - presence and concentration of each type of additive (IEC 60296 clause 5.4);
B. Absence of DBDS (DiBenzylDiSulfide < 5mg/Kg) and/or other types of "Corrosive Sulfur" compounds in accordance with method IFED with GC-AED&MS technique;
C. "Potentially Non Corrosive" compliance with IEC 65535 (CCD) and "DownSize" Test, 150°C, 48 hours-ASTM 1275-B
D. Total Corrosive Sulfur – SM-TCS <3 mg/Kg
E. Copper Deposition Test (on the CCD paper) with ICP

Solutions > Countermeasure no. 2 (1/3)
For Unused Oil, inspection in tanks and drums

A. Compliance of the oil with the specifications and standard IEC 60296 Third edition 2003-11
B. Compliance of the oil with the specifications for the presence and concentration of additives (anti-oxidants, passivators etc.);
C. Compliance for the absence of DBDS (DiBenzylDiSulfide < 5mg/Kg) and/or other types of corrosive compounds in accordance with method IFED with HRGC-AED&MS technique
D. "Potentially Non Corrosive" compliance with IEC 65535 (CCD) and "DownSize" Test, 150°C, 48 hours-ASTM 1275-B
E. Total Corrosive Sulfur – SM-TCS <3 mg/Kg
F. Copper Deposition Test (on the CCD paper) with ICP
G. "Oil Fingerprint Profile SM-IFED" with HRGC-AED & MS technique
### Copper Deposition Test

Tests on Cigre’s RRT oils, copper quantified by ICP-AES. 
\[ \text{[Cu]} = \text{mg/Kg} \]

#### IEC TC10 WG 35
Maina R., Tumiatti V.

#### Solutions > Countermeasure no. 2 (2/3)

<table>
<thead>
<tr>
<th>CIGRE</th>
<th>Cu</th>
<th>kd</th>
<th>S</th>
<th>DBDS</th>
<th>Naphthenic</th>
<th>Corrosive</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>139</td>
<td>1.11</td>
<td>Non corrosive</td>
<td>&lt;5 mg/Kg</td>
<td>Naphthenic</td>
<td>Passivated</td>
</tr>
<tr>
<td>3</td>
<td>11.46</td>
<td>31.27</td>
<td>Not corrosive</td>
<td>4.08</td>
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<td>Passivated</td>
</tr>
<tr>
<td>4</td>
<td>20.04</td>
<td>2.29</td>
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<tr>
<td>5</td>
<td>255.2</td>
<td>31.27</td>
<td>Not corrosive</td>
<td>10.08</td>
<td>Naphthenic</td>
<td>Passivated</td>
</tr>
<tr>
<td>6</td>
<td>255.2</td>
<td>31.27</td>
<td>Not corrosive</td>
<td>10.08</td>
<td>Naphthenic</td>
<td>Passivated</td>
</tr>
<tr>
<td>7</td>
<td>255.2</td>
<td>31.27</td>
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<td>&lt;5 mg/Kg</td>
<td>Naphthenic</td>
<td>Passivated</td>
</tr>
<tr>
<td>8</td>
<td>255.2</td>
<td>31.27</td>
<td>Not corrosive</td>
<td>10.08</td>
<td>Naphthenic</td>
<td>Passivated</td>
</tr>
<tr>
<td>9</td>
<td>255.2</td>
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<td>&lt;5 mg/Kg</td>
<td>Naphthenic</td>
<td>Passivated</td>
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<tr>
<td>10</td>
<td>255.2</td>
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<td>10.08</td>
<td>Naphthenic</td>
<td>Passivated</td>
</tr>
<tr>
<td>11</td>
<td>255.2</td>
<td>31.27</td>
<td>Not corrosive</td>
<td>&lt;5 mg/Kg</td>
<td>Naphthenic</td>
<td>Passivated</td>
</tr>
<tr>
<td>12</td>
<td>255.2</td>
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<td>10.08</td>
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<td>Passivated</td>
</tr>
<tr>
<td>13</td>
<td>255.2</td>
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<td>Not corrosive</td>
<td>&lt;5 mg/Kg</td>
<td>Naphthenic</td>
<td>Passivated</td>
</tr>
</tbody>
</table>

#### Solutions > Countermeasure no. 2 (3/3)

**Correlation between copper deposited on the paper and Corrosive Sulfur**

- **CIGRE 3**
  - Cu = 3909 mg/Kg
  - kd = 31.27
  - S - Non corrosive
  - Naphthenic
  - DBDS = <5 mg/Kg

- **CIGRE 1**
  - Cu = 139 mg/Kg
  - kd = 1.11
  - S - Non corrosive
  - Naphthenic
  - Passivated
  - DBDS = 168 mg/Kg

- **CIGRE 13**
  - Cu = < 125 mg/Kg
  - Corrosive
  - Naphthenic
  - DBDS = 234 mg/Kg

**Conclusion:**

Other corrosion mechanism of copper (?) not correlated to Corrosive Sulfur Compounds!
Prescriptions for the supply of oil for first impregnation

A. Compliance of the oil with the specifications and standard IEC 60422 Third edition 2005-10
B. Compliance of the oil with the specification for the presence and concentration of additives (anti-oxidants, passivators etc.);
C. Compliance for the absence of DBDS (DiBenzyDiSulfide < 5mg/Kg) and/or other types of corrosive compounds in accordance with method IFED with HRGC-AED&MS technique
D. "Potentially Non Corrosive" compliance with IEC 65535 (CCD) and "DownSize" Test, 150°C, 48 hours-ASTM 1275-B
E. Total Corrosive Sulfur – SM-TCS <5 mg/Kg

CASE HISTORY:
IFED: fingerprinting of new oil
DBDS cross contamination “Factory Test”

This batch of oil fails CCD
For Oil and equipment in operation

A. Compliance with standard IEC 60422 Third edition 2005-10, clause 9 Table 3

B. Integrating management requisites for each equipment and charge of insulating oil with specific tests and monitoring:
- presence and concentration of every type of additives (IEC 60296 Ed 3 2003-11 clause 5.4)

C. Compliance for the absence of DBDS (DiBenzyldiSulfide < 5 mg/Kg) and/or other types of corrosive compounds in accordance with method IFED with HRGC-AED&MS technique

D. "Potentially Non Corrosive" compliance with IEC 65535 (CCD) and "DownSize" Test, 150°C, 48 hours-ASTM 1275-B

E. Total Corrosive Sulfur – SM-TCS <3 mg/Kg

Management of oils in operation, sampling, tests, corrective actions and treatment of the oils

A. Compliance with standard IEC 60422 Third edition 2005-10, clause 10, 11,12 tables 4, 5, 6);

B. Compliance with the specification for the presence and concentration of additives (anti-oxidants, passivators etc.);

C. Compliance for the absence of DBDS (DiBenzyldiSulfide < 5mg/Kg) and/or other types of corrosive compounds in accordance with method IFED with HRGC-AED&MS technique

D. "Potentially Non Corrosive“ compliance with IEC 65535 (CCD) and "DownSize“ Test, 150°C, 48 hours-ASTM 1275-B

E. Total Corrosive Sulfur – SM-TCS <3 mg/Kg;

F. Compliance with dissolved gases (DGA) in accordance with IEC 60567, IEC 60599, furanic compounds, dissolved metals, particles etc.

G. Compliance of furanic compounds with standard IEC 61198;

H. Oil treatment and corrective actions in accordance with clause 12 tables 5, 6.
Metal passivating additives for oil in operation with BenzoTriAzoles (BTA) and derivatives

Ciba-Irgamet 39® NyPass

A. Metal passivators are not able to decompose the DBDS and corrosive sulfur compounds and "is not a guarantee against failures" (CIGRE A2.32 Art. 4.1 Mitigation techniques. Metal passivators page 19)

B. Sampling and monitoring of passivating additives after each oil treatment performed in compliance with standard IEC 60422 Third edition 2005-10 art 12 (reconditioning, reclamtion, dehalogenation). It is known that under normal vacuum and/or reclamation conditions, the concentration of passivating additives (100 mg/Kg) is considerably reduced if not eliminated, depending upon the type of process, operational temperature and pressure;

C. Tests and monitoring of the concentration of passivating additives through time.

Typical metal passivator additive

Ciba Irgamet 39®

Case history is reported "In a population of 21 transformers, preventive action was taken in July and August 2005. Because of the shortage of safe oil, only five reactors could be retrofilled and the remaining 16 were passivated. As of December 2006, eight of the latter group failed in service, respectively at 33, 102, 136, 168, 284, 363, 478, and 590 days after passivation. No failure have so far occurred for any of the retrofilled units in this group" (CIGRE A2.32 Oil exchange, art. 4.3 pag.25)
Example of stray gassing following the passivation with Ciba Irgamet 39

Decay of Ciba Irgamet 39 and its effect on oil’s corrosiveness
Risks correlated to passivating additives 
BenzoTriAzoles (BTA) and derivatives

To evaluate the compliance with European regulation 1907/2006 of 18/12/2006 "REACH" (Registration, Evaluation and Authorization of Chemicals) and the safety requisites of IEC TC111 and IEC Guide 109 WG 16, approved during the Plenary Meeting 2000 in Geneva.

Risks correlated to the by-products of BenzoTriAzoles and derivatives

To evaluate the type and concentration of the decomposition substances generated by partial discharges, long-term thermal stress and pyrolysis under uncontrolled reaction conditions on the various catalytic surfaces (ex. iron, copper, etc.)
Risks correlated to the by-products of BenzoTriAzoles and derivatives

“Studies have pointed out that benzotriazole is mutagenic in in-vitro bacterial cellules, but not in the mammal cellular systems. The report does not provide conclusions, but defines that benzotriazole must be considered as a “suspect human carcinogen”.


Irgamet 39®

Chemical nature: Isomeric mixture of isomerica N,N-bis(2-etilesil)-4-metil-1H-benzotriazol-1-metilammina e N,N-bis(2-etilesil)-5-metil-1H-benzotriazol-1-metilammina (Numeri CAS: 80584-90-3, 80595-74-0)

Numero CAS 80584-90-3 + 80595-74-0

**Indication of dangers**

Classified as **dangerous** in accordance with EC Directives

- **N** Dangerous for the environment

- **Xi** Irritant

It requires the implementation of special Fire Prevention Measures
A. DBDS and corrosive sulfur compounds can be decomposed from the oils with "Selective Depolarisation (a combination of reagents and sorbents)". (…) in "Continuous on-line treatment" (CIGRE A2-32 art. 4.2 page 25).

B. Multi-functional decontamination and depolarisation of oil and equipment (including dissolved metals that cannot be eliminated by a normal reclaiming process) capable also of reinstating the insulating properties of the oils in accordance with standard IEC 60422 Ed. 3 2005-10 clause 12 and table 5.

C. Additivation (if required) of the oil with oxidation inhibitors type DBPC at 0,3% in weight.

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**Chemical decomposition of DBDS with selective depolarisation process**

![Graph showing concentration of DBDS and Irgamet 39](image)
DMU (Decontamination Mobile Unit) for "On Load Selective Depolarisation Process"

Selective Depolarisation and DBDS elimination

Effect of the CHEDCOS® selective depolarisation process: chemical decomposition of corrosive compounds “DBDS”
### Solutions > Countermeasure no. 7 (5/6)

Typical results for “On-Load selective depolarisation process” – GSU transformer 192 MVA 400KV

<table>
<thead>
<tr>
<th>Item</th>
<th>Parameters analysed</th>
<th>Unit of measure</th>
<th>Initial values (15/12/2006)</th>
<th>Final values 25/01/2007</th>
<th>Contractual warranty</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Corrosive sulfur</td>
<td>-</td>
<td>4a</td>
<td>2a</td>
<td>&lt;2e</td>
</tr>
<tr>
<td>2</td>
<td>DiBenzDithi Alfred</td>
<td>mg/kg</td>
<td>110</td>
<td>&lt;5</td>
<td>&lt;10</td>
</tr>
<tr>
<td>3</td>
<td>Dissolved water</td>
<td>mg/kg</td>
<td>12</td>
<td>6</td>
<td>&lt;10</td>
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<tr>
<td>4</td>
<td>Combustible gases</td>
<td>µL</td>
<td>327</td>
<td>N.D.</td>
<td>&lt;300</td>
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<tr>
<td>5</td>
<td>Breakdown voltage</td>
<td>kV</td>
<td>-</td>
<td>75</td>
<td>60</td>
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<tr>
<td>6</td>
<td>Neutralisation number</td>
<td>mg KOH/g</td>
<td>0.333</td>
<td>&lt;0.01</td>
<td>&lt;0.05</td>
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<tr>
<td>7</td>
<td>Dielectric dissipation factor</td>
<td>-</td>
<td>0,0180</td>
<td>0.0180</td>
<td>&lt;0.10</td>
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<tr>
<td>8</td>
<td>Poly Chlorinated Dibenyls</td>
<td>mg/kg</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
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<tr>
<td>9</td>
<td>Particles</td>
<td>Cod. Imp</td>
<td>22/17/11</td>
<td>15/13/10</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>Colour</td>
<td>ASTH scale</td>
<td>3</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>11</td>
<td>Interfacial tension</td>
<td>mN/m</td>
<td>17.6</td>
<td>31.6</td>
<td>-</td>
</tr>
<tr>
<td>12</td>
<td>Bionoam89</td>
<td>mg/kg</td>
<td>46</td>
<td>&lt;3</td>
<td>-</td>
</tr>
</tbody>
</table>

### Solutions > Countermeasure no. 7 (6/6)

Case history > 100 transformers for “On-Load & Off-load selective depolarisation process”

![Case history: Selective depolarisation of corrosive sulfur](image)
Oil Exchange

To guarantee DBDS concentration < 10 mg/kg (after 90 days) it is necessary to exchange the oils twice.

The typical concentration of the DBDS in "Unused mineral insulating - Naphthenic Base with DBDS" is 150-250 mg/Kg. This oil change evidently reduces the corrosive compounds content of the oil, diluting them accordingly with the ratio between the new oil added and the remnant old oil (which results from the addition of the oil adsorbed on the active part and the oil remaining in the bottom of the tank).

That typical ratio may be 10% (CIGRE A2.32-art. 4.3 pag. 25) or more, depending on the amount of paper and other adsorbing materials, and on the shape of the tank also. When the oil is to be changed, a preventive test of corrosive sulfur on a suitable mixture of the old and the new oil should clarify if the mitigation action will be adequate to obtain finally a non corrosive oil.

Crossed contamination of used oil by DBDS (bulk reclamation)

<table>
<thead>
<tr>
<th>Sample</th>
<th>mg/Kg DBDS</th>
<th>Corrosive sulphur</th>
</tr>
</thead>
<tbody>
<tr>
<td>1b</td>
<td>20.95</td>
<td>4a</td>
</tr>
<tr>
<td>1a</td>
<td>22.00</td>
<td>4a</td>
</tr>
<tr>
<td>2b</td>
<td>22.52</td>
<td>4a</td>
</tr>
<tr>
<td>2a</td>
<td>13.65</td>
<td>4a</td>
</tr>
<tr>
<td>3b</td>
<td>50.04</td>
<td>4a</td>
</tr>
<tr>
<td>3a</td>
<td>14.03</td>
<td>4a</td>
</tr>
<tr>
<td>4b</td>
<td>12.64</td>
<td>4a</td>
</tr>
<tr>
<td>4a</td>
<td>17.75</td>
<td>4a</td>
</tr>
<tr>
<td>5b</td>
<td>15.47</td>
<td>4a</td>
</tr>
<tr>
<td>5a</td>
<td>12.46</td>
<td>4b</td>
</tr>
</tbody>
</table>

Concentration of dibenzyl disulfide in samples before (b) and after reclamation (a). GC-MS and GC-ECD analyses.

1 According to ASTM 1275 B (150°C, 48 h)
Replacement of windings-spare parts

A. The corrosion process and the formation of copper sulfides are irreversible. The Selective Depolarisation and oil exchange are not able to eliminate the deposit trapped on insulating papers and windings.

B. The deposit of copper sulfides accumulated does not modify the DP of papers, but modifies, in an irreversible manner, the insulating electric properties that could become critical.

C. Under this critical condition, it is necessary to replace the components, the windings and/or the equipment.

No-Sulfur Corrosion and Effects on losses
Copper content in corrosive and non-corrosive oils

![Graph showing copper concentration over ageing time](image)

- Oil 1 - Naphtenic HG - Type I - NC
- Oil 2 - Paraffinic StdG - Type U - NC
- Oil 3 - Naphtenic StdG - Type U - C
- Oil 3 - Naphtenic StdG - Type U - C (+ Air)

Copper deposited on paper surface

![Graph showing copper deposition over ageing time](image)
Copper in oil before and after oil exchange

Copper in oil and DDF decay after oil depolarization
Case history of Selective Depolarisation of organo-metallic compounds in oil

### Solutions > Countermeasure no. 10 (6/6)

**KEY PARAMETER:**
Copper, delta tg

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Before</th>
<th>After</th>
<th>Value IEC limit 60422</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total dissolved gases (%)</td>
<td>0.06</td>
<td>1.43</td>
<td>-</td>
</tr>
<tr>
<td>Moisture (mg/kg)</td>
<td>14</td>
<td>11</td>
<td>&lt; 20</td>
</tr>
<tr>
<td>Dissipation factor (delta tg)</td>
<td>1.198</td>
<td>0.072</td>
<td>&lt; 0.1</td>
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<tr>
<td>TAN (mg CO&lt;sub&gt;2&lt;/sub&gt;/g)</td>
<td>0.213</td>
<td>&lt; 0.03</td>
<td>&lt; 0.15</td>
</tr>
<tr>
<td>Colour</td>
<td>3.5</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td>Breakdown voltage (kV)</td>
<td>66</td>
<td>74.1</td>
<td>&gt; 60</td>
</tr>
<tr>
<td>Breakdown voltage Copper in oil</td>
<td>nd</td>
<td>15/13</td>
<td>&lt; 17/14</td>
</tr>
<tr>
<td>Rame in olio (mg/kg)</td>
<td>43.1</td>
<td>12.3</td>
<td>-</td>
</tr>
</tbody>
</table>

The "DBDS & Corrosion Free Program" is able to prevent and/or mitigate the "Corrosion Phenomena".

The countermeasures suggested represent the Best Available Techniques (BAT) for the Life Cycle Management (LCM) of strategic electrical equipments filled with mineral insulating oils.

### Conclusions
Thank you for your kind attention

Q & A

World Wide Sustainable Solutions for our Future

“We are the products of the Environment where we live and work”

Vander Tumiatti
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Sea Marconi Technologies

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