

# Conditions for DBDS Induced Corrosive Sulfur Formation.

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**Abstract**—The conditions required for the formation of copper sulfide originating from the DBDS oil additive which was identified by Scattigio (Terna, Italy) in 2005 is: “sufficiently high copper temperature” and copper corrosion will appear. This paper describes the findings when a transformer allegedly failed by corrosive sulfur was inspected with regards to the presence of copper corrosion. Strong corrosive attacks were found and their relation to temperature was very evident.

**Keywords**-component; Copper corrosion, Arrhenius Equation, trigger temperature, DBDS, distribution, catalytic induced, copper passivator.

## I. INTRODUCTION

Formation of corrosive sulfur follow the relation presented by *Svante Arrhenius* in 1898 [1], the so called *Arrhenius Equation* which state the relation between the few parameters that govern the formation rates of different chemical species.

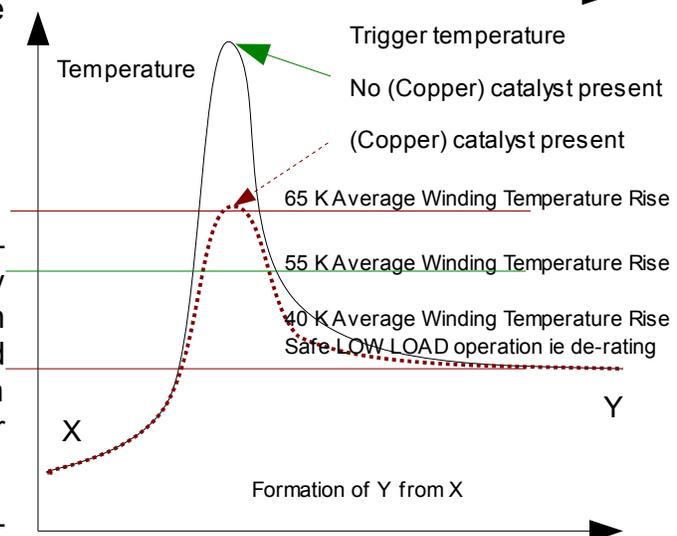
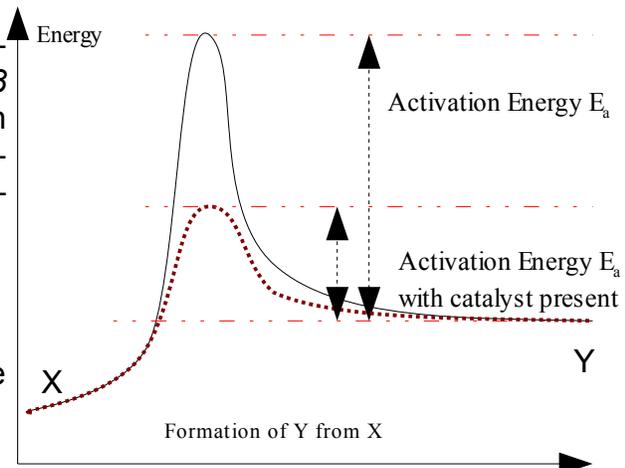
$$d[C]/dt = A \cdot e^{(-E_a/RT)}$$

Where  $d[C]/dt$  is the concentration change by time of chemical species.

- A is a statistical parameter (chance for collision between reactants).
- R is the universal gas constant.
- T is the absolute temperature.(K).

$E_a$ , (Activation Energy) was a concept introduced by Arrhenius to explain e.g. why catalysts had such a profound effect on chemical reaction rate and can be defined as follows: “The energy barrier over which a reaction system must progress in order for reactants to form products”.

Energy on a molecular level is often described by different modes of vibration



(amplitude and frequency). The simplest way is of course what we can measure macroscopically e.g. temperature or pressure.

The general energy level of a molecule thus increase by temperature so in a simplified scheme temperature can replace the label "Energy".

Gas formation and formation of any chemical compounds in the transformer is essentially the transfer of electrical losses of energy to chemically stored energy and thus the total energy level increase of the hydrocarbons present in a transformer reflect the energy loss inside the transformer unit.

## II. THE FAILED TRANSFORMER

Hydroelectric power plant. Transformer data:

1999 GSU.	75 MVA 11/220 kV.
Oil weight: 36000 kg.	Oil make Shell Diala DX.
Cooling ONAF.	The unit is sealed.

DBDS was determined to be 110 mg/kg.

It is known that Shell insulating oil formulation patent requires 200 mg/kg. [7]

## III. HV FAILED WINDING.

The failure is a local winding to winding flash over which is typical for di-electrical insulation collapse failures,

One high voltage winding had failed and was therefore accessible for inspection and sampling.

The design layout was 84 axial winding levels and 26 radial winding layers.

Samples were taken from

1. Layer 7 from the bottom where the oil was expected to be fairly cool .
2. Layer 37, 7 layers below the failure.
3. Layer 49, 7 layers above the failure.
4. Layer 77 from bottom (7 below top layer).

The samples taken were 200 mm pieces of the winding including paper insulation. All 26 radial layers were sampled totaling 104 pieces of winding.

## IV. OCULAR INSPECTION OF SAMPLES.

The cellulose of the samples specimens was stripped and the inner cellulose layer was inspected for deposits. None were found on the (1.) but on (4.) all cellulose inner layers displayed deposits that had evidently come lose from the copper conductor.

This scaling of copper sulfide is due to the very different volume expansion coefficients of metals to minerals (copper sulfide) and the weak bonding to the metal surface.

(2.) showed some variation in copper sulfide formation while (3.) showed very little variation. None showed any deviation from the expected result.

### V. COPPER SAMPLES PREPARATION AND INSPECTION.

Pieces of 35 mm were cut off and degreased using petroleum ether and dried before inspecting in scanning electron microscope.

At random a large number of SEM-analyses were made and they confirmed that the basic deposit had the same atomic distribution as expected from copper sulfide. This is a strong indication that the deposits may be copper sulfide.

As all samples from layer 7 from bottom were shiny only 7 out of the 26 were investigated in SEM.

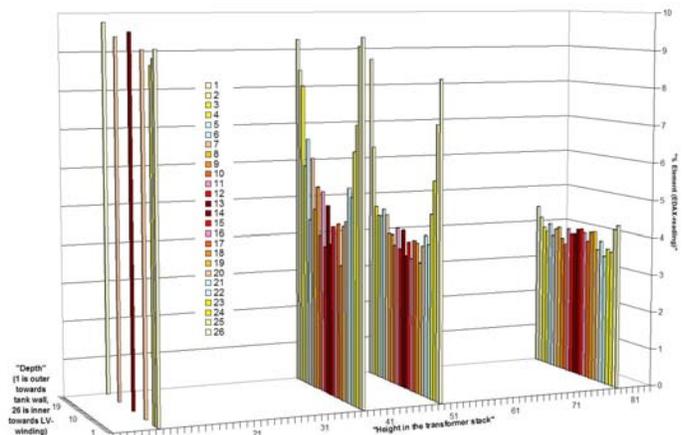
### VI. SURFACE OXYGEN, COPPER & SULFUR DISTRIBUTION.

Oxygen has a very strong tendency to adsorb on a copper surface. This is one of the major reason why antioxidants are of such interest in transformers where the copper surface is naked to oxygen. Oxidation reactions will be very pronounced if temperatures are elevated and no antioxidant protection exists.

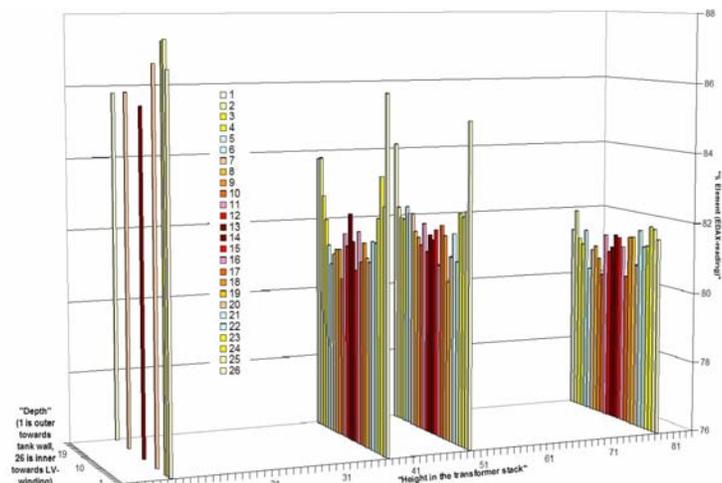
When the copper surface becomes hot, oxygen reacts and as the resulting reaction product desorbs from the surface it is replace by what is present in the empty location's neighborhood (e.g. a DBDS molecule may replace it and the formation of copper sulfide is under way).

The adsorbed oxygen is unreacted and remain on the conductor surface on the lower winding levels but the higher up in the winding stack the less oxygen is left unreacted.

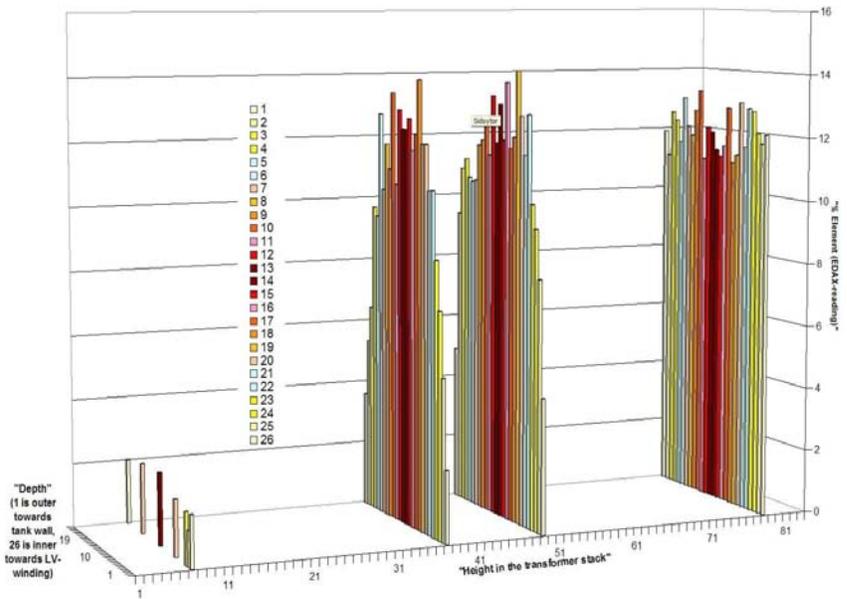
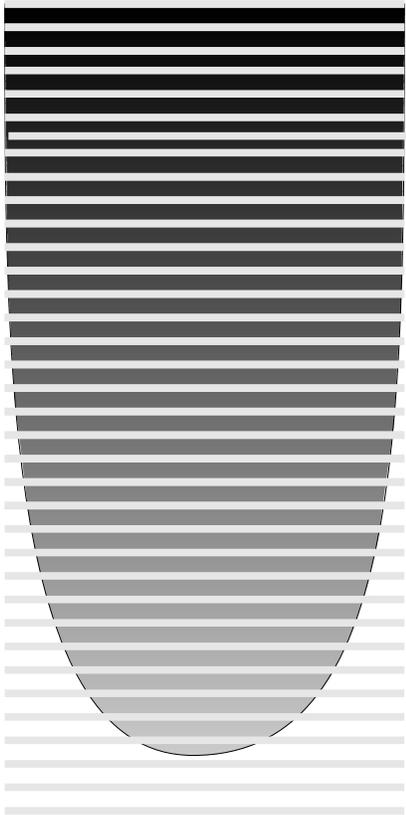
Very little sulfidation on the lower layer and on the radially innermost and outer-most of the windings except for the top layer which has an even and complete copper sulfide covering .



Oxygen fraction in (%) on conductor surface.



Copper distribution as measured in SEM (EDAX).



*Sulfur distribution.*

The distribution is evidently completely in agreement with the temperature distribution expected for a transformer.

Low temperature; no sulfidation attack, high temperature (active copper); strong sulfidation attacks.

If the operating temperature would have been at this level or less, **the transformer would not have failed due to copper corrosion**.

### VII. PHOTOGRAPHIC REPRESENTATION.

The picture and sketch speaks for themselves; **the temperature influence is obvious.**



Pieces of copper winding taken from different "heights" in a stack of winding in a transformer supposedly failed due to corrosive sulfur (manufacturers statement). It must be pointed out that the fault section of this transformer was not available for for us to inspect. 104 different winding sections were diagnosed.

If the copper surface would have been enameled no corrosion attacks would have been possible.

## VIII. CONCLUSIONS.

Oil additives in conjunction with high local operating temperatures are the true reasons behind the copper sulfidation plague that has struck the power producing and distribution industry.

The “discovery” of DBDS as additive in oil in 2005 [4] in combination with screening tests made and which reveal that DBDS has been used for decades give the true picture of the problem.

DBDS was once selected to boost oil performance and its transition to corrosion agent was propagated by the increase in copper temperatures which have been the result of design criteria changes in the 1980's. Thus, it is difficult to find this problem in transformers older than 1980. They may contain DBDS but DBDS at low temperatures is an active antioxidant, at medium temperatures it is sludge forming and at high temperatures it is corrosive.

DBDS has been known by and used by oil companies for a very long time and its corrosive (metal-reactive) properties have been utilized in lubricants. It has been well researched [5,6] and is NOT a naturally appearing compound in oils (due to its extreme reactivity).

As the temperature correlation is so obvious the consequence is also that copper passivators will not be a solution to the problem. On the hot surfaces the copper passivator is quickly consumed and thus the protection gone.

In summary: it will not work if you need it (i.e. if you have hot surfaces). If you do not have hot surfaces you don't need copper passivators....

## IX. . REMAINING WORK.

The next paper in this series will report the trigger temperature for DBDS i.e. make possible to find the “safe” operating condition for a unit in service that has the additive DBDS at risk concentrations.

From the development of the CCD test it is however evident that the trigger temperature is below 150 °Celsius and from the fact that oils were not corrosive previous to the CCD test development.

However it also remains to find methods to establish level of risk for different types of transformer designs e.g. by shear design aspects shell type designs must be more vulnerable than core type designs and ONAN type of cooling must more resistant to corrosive attacks from the DBDS additive than those of ODAF or OFAF. Reactors must be more of a risk object than transformers, again for design reasons.

It is also necessary to screen the transformer population to identify and act on the individuals which, from DBDS content, design aspects, mode of operation and operating parameters are to be considered a risk.

It is also appropriate to device an insulating oil standard that does not allow the use additives without declaring them to the transformer owner.

The positive effect of the DBDS aspect is that it has identified a number of erroneously designed transformer types.

## X. ACKNOWLEDGEMENTS.

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## XI. REFERENCES

- [1] Arrhenius, Svante. "Zur Theorie der chemischen Reaktionsgeschwindigkeit". Stockholm, 1898. First edition.
- [2] Bylaite Egle, Arvidsson Lars: Corrosive sulphur. Observations and interpretations from a large number analyses. Part 2: Dielectric aspects. GCC Cigré November 2007 Dubai.
- [3] Griffiths, David (1999) [1981]. "7. Electrodynamics". in Alison Reeves (ed.). Introduction to Electrodynamics (3rd edition ed.). Upper Saddle River, New Jersey: Prentice Hall. pp. 286. ISBN 0-13-805326-x. OCLC 40251748.
- [4] Riccardo Maina, Fabio Scatiggio, Shubhen Kapila, Vander Tumiatti, Michela Tumiatti, Massimo Pompilli: Dibenzyl disulfide (DBDS) as corrosive sulfur Contaminant in used and unused mineral insulating oils. (Personal communication with F. Scatiggio).
- [5] D. STOYCHEV, I. VITANOVA, R. BUYUKLIEV, N. PETKOVA, I. POPOVA, I. POJARLIEV. JOURNAL OF APPLIED ELECTROCHEMISTRY 22 (1992) 987-990. Effect of the structure of aromatic disulphides on some physico-mechanical properties of electrodeposited copper coatings. (Institute of Physical Chemistry and Institute of Organic Chemistry: Bulgarian Academy of Sciences, 1040 Sofia, Bulgaria).
- [6] N. A. Kudryavtseva, N. I. Lulova, A. A. Fufaev, and S. B. Borshchevskii. PYROLYTIC GAS CHROMATOGRAPHIC PROCEDURE FOR DETERMINATION OF THERMAL Stability of Sulfur-containing Additive (Di-Benzyl Di-Sulfide) and Composition of Additive De-Composition Products. (Translated from Khimya i Tekhnologiya Topliv i Masel, No. 3, pp. 59-61, March, 1977.)
- [7] World Intellectual Property Organization WO 2006/136594 A1 (28.12.2006). Shell Internationale Research Maatschappij B.V. Carel van Bylandtlaan 30 NL 2596 The Hague. Andree Hilker, Volker Null (DE).

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Lars Arvidsson, born 1954. He graduated from the University of Technology in Lund Sweden 1979. M Sc in Chemical Process Engineering.

Mr Arvidsson has been employed with ASEA, ABB and Vattenfall in Sweden.

He is the founder, owner and General Manager of VPdiagnose/ Västerås Petroleum-Kemi AB (1994).

