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«Hvor fåfengt menneskene gjennom alle tider har kjempet mot naturen! Tilsynelatende kan de nok overvinne og beherske den, heve seg over dens lover, men naturen kapitulerer aldri.»

Hans Børli (1918- 1989)

Til Mor og Far

Summary

Breakdowns in high voltage transformers are of major concern. It is therefore a goal to prevent this from happening. Chemical degradation (e.g. oxidation, hydrolysis and corrosion) of the insulation systems and windings and formation of deposits are some of the most important causes of breakdowns in oil-paper insulated transformers.

Several of the methods for studying the oxidation stability of dielectric liquids are time consuming and involve harsh conditions, far from the conditions in the transformer. Some of the methods expose the sample to oxygen flow and uses high temperature. In this work the aim has been to find a quick and suitable method for studying oxidation stability of dielectric liquids under more realistic conditions, with regard to the oxygen and temperature. By using an isothermal microcalorimeter dielectric liquids and model liquids have been studied in terms of the oxidation stability.

This work demonstrates that the isothermal microcalorimeter is well suited for the study of oxidative stabilities of dielectric liquids. The experiments were performed at 120, 110 and 90°C in the isothermal microcalorimeter. The area (integral) below the curves provided by the calorimeter (heat flow vs. time) was found to correlate to the ratio of the volume of the sample over the volume of the head space (amount of available air to the sample). The area below the curves also correlated with the type of oil. It was seen that mineral oil without any additives to stabilise the oil had a much larger area below the curve than the inhibited oil (with additives).

16 unknown dielectric liquids from a Round Robin test were studied with regard to the oxidation stabilities and classified as having high stability, medium, low, very low and extremely low stability by using the area below the curves. Since these samples came from a Round Robin test, the results could be compared with results of investigation of the same unknown liquids by other laboratories that used other methods for determination of the oxidation stability of the dielectric liquids. The results, from the participant laboratories in the Round Robin test that use methods based on the same conditions (observing the onset of the oxidation), agree very well with the results obtained in the isothermal microcalorimeter method, used in this work (based on measuring the integral of the isotherm from the calorimeter).

The isothermal microcalorimeter was also used to study the effect of copper (solid), dibenzyl disulphide and a commercial metal passivator on the oxidation of a hydrocarbon liquid (hexadecane as model oil). This was also done with a vegetable oil and mineral oils. The catalytical effect of copper on the oxidation of the hydrocarbon was observed. The catalytical effect was clear in a base oil with no added antioxidants, passivators or deactivators. The effect of DBDS as antioxidant was also evident in these experiments. The catalytical effect of copper was evident only using a certain amount. Increasing the amount of copper beyond this level removed the catalytical effect. This is sometimes referred to as the critical phenomenon in catalysis.

Also a metal passivator that is used in transformers for preventing corrosion on the copper has been study to better understand the effect of this passivator. Experiments where copper strips were aged in corrosive oil with and without a metal passivator at 150°C over different time showed that the passivator has no effect if added to an aged system where the formation of copper-sulphide has started on the metal surface. The decrease in the concentration of sulphur (measured with potentiometric titration) with time is larger in the samples not added the passivator from the start of the experiment, indicating that the sulphur species reacts with the copper. The effect of adding the passivator before ageing was very good. The effect of the metal passivator Irgamet39 (I39) may be reduced by possible reaction with oxidation products in an aged oil.

Experiments where the passivator was studied were also performed. The change in the concentration (measured with UV-Vis spectrophotometer) of the I39 when heating the solution with the I39 in presence of a copper coupon was measured. The adsorption of the passivator on the copper appeared to increase with increasing temperature. The adsorption of the metal passivator on copper was also studied using a quartz crystal microbalance (QCM) with copper. This gave an indication of the adsorption of a monolayer and multilayers on the copper. The results showed that the adsorption is dependent on the solvent.

Acknowledgements

There are so many people that I want to thank for all the support and help. Without all these people this thesis would not be possible.

I want to thank my supervisor Edd Anders Blekkan at the Norwegian University of Science and Technology (NTNU) and Marit-Helen Glomm Ese my supervisor at SINTEF Energy Research. Without you I would be stranded.

I also have to direct huge thanks Lars Espen Lundgaard and Marit-Helen at SINTEF Energy Research for giving me the opportunity to do this PhD. It has meant a lot to me.

Most of the work has been performed at SINTEF Energy Research, I am so grateful for the opportunity to use the laboratories and having my office at SINTEF. I want to thank all my former and present colleagues at SINTEF for constructive and interesting professional talks, but also for all the laughs I have had with you. I want to thank Knut Brede Liland and Dejan Susa for the help and support on the work with the calorimeter and transformer theory and for all other support. Thanks to Cecilie, Dag, Espen, Frank, Hans Helmer, Jorunn, Mildrid, Murside, Stian, Svein Magne, Sverre, Torbjørn and Øystein for being so good colleagues.

I want to thank Carl Marius Roel and his supervisor Wilhelm Robert Glomm at the Department of Chemical Engineering at NTNU for choosing the project on corrosive sulphur and accomplish it so well.

I will also thank all the financial supporters that have made this PhD possible.

A special thank goes to my friends and family for all the support. Thanks to my “chemical friends”; Asmira, Elisabeth, Kristina, Marion, Marit, Silje and Solveig. Thanks to my friends Mari and Nina. From all of my hart thanks to my parents Gunn and Bjørn Tronstad for believe in me and giving me the background that I have needed to perform this work.

A grateful thank to my most important and fantastic persons in my life; Øystein Knauserud and our son Sverre. I thank you for holding out with me during this work, for believe in me and supporting me, you mean all to me!

Preface

This PhD thesis contains the results of my research at the Department of Chemical Engineering at the Norwegian University of Science and Technology (NTNU) and SINTEF Energy Research in the period from autumn 2008 to autumn 2012. The work was carried out with Edd Anders Blekkan from the Department of Chemical Engineering and Marit-Helen Glomm Ese from SINTEF Energy Research as supervisors.

This research was financed through the KMB project "Thermal and electromagnetic performance of transformers" (project number 173142). This KMB project was a joint effort between Statnett, Hafslund, Statkraft, EDF, ABB, Nynäs, Siemens, Norwegian Water Resources and Energy Directorate (NVE) and The Research Council of Norway, where the research work was done by SINTEF Energy Research.

The measurement of the density of dielectric liquids was performed by the summer student at SINTEF Energy Research, Delphine Laurichesse.

The measurements performed with a quartz crystal microbalance (QCM) and UV-vis spectrophotometer were mainly performed by Carl Marius Roel as master student at the Department of Chemical Engineering at NTNU under supervision of Associate Professor Wilhelm R. Glomm, Professor Edd A. Blekkan and me (PhD candidate Ingvild Tronstad) from August 2009 to May 2010. These results are included in the paper III in this thesis.

List of papers

This thesis is based on the following three papers:

Paper I
Ingvild Tronstad, Edd A. Blekkan, Marit-Helen G. Ese 2012. "Isothermal microcalorimetry as a tool for studying oxidation stability of insulating liquids." IEEE Transactions on dielectrics and electrical insulations 2012 Volume 19 Number 5 Page: 1528-1536.

Paper II
Ingvild Tronstad, Marit-Helen G. Ese, Edd A. Blekkan. ”A Study of the Effect of Copper and Additives in Hydrocarbon and Ester Based Insulating Liquids with Isothermal Microcalorimetry”. Submitted IEEE Transactions on dielectrics and electrical insulations.

Paper III
Ingvild Tronstad, Carl Marius Roel, Wilhelm R. Glomm, Marit-Helen G. Ese, Edd A. Blekkan: “Ageing and Corrosion of Paper Insulated Copper Windings: The Effect of Irgamet39 in Aged Insulated Oil”. Submitted IEEE Transactions on dielectrics and electrical insulations.

Contents

List of Symbols

dQ/dt		Rate of heat production by the sample (J/sec)
Φ		Heat exchange with the surroundings (W)
dt		Change in time
dT		Change in temperature (K or ^{o}C)
C	(calorimeter eq.)	Heat capacity (J/K or ^{o}C)
Δm		Change in mass
C	(Sauerbrey eq.)	Sauerbrey constant
n	(Sauerbrey eq.)	Overtone
ΔF		Frequency change
E_{cell}		Energy of the cell
K		A constant including the activity of the inner solution and the number of molecules
f_{start}		frequency at start
f		Frequency
ΔG		Gibbs energy
ΔH		The change in enthalpy
ΔS		The change in entropy
T		Temperature
R		The universal gas constant (8,134 J/K mol)
$a_{i,sample}$		The activity of the sample
$a_{i,int.soln}$		The activity of the intern solution in the electrode
E		The energy
n		Number of electrons transferred
F		Faradays constant
a_i		The activity of the ion
z_i		The charge of the ion
log T		Transmittance
P		Outgoing radiation
P_o		Ingoing radiation

1 Introduction

1.1 Motivation

The modern human society depends on electricity to function. Everything from hospitals to traffic lights is dependent of a safe supply and a stable voltage. In transfer of electric power the losses in the lines is proportional to the square of the current. It is therefore important to keep the current as low as possible and the voltage corresponding high. Domestic suppliers are provided at lower voltages, relying on transformers; the role of the transformer is to transfer energy and change the voltage without changing the frequency. All equipment from mobile phone chargers to power grids depends on transformers. For supply of electricity from the power plant to the power grid and further to the domestic household the transformers are essential to secure the availability (Aasen 1995).

High voltage (HV) transformers consist of a laminated iron core and insulated windings or groups of windings. This core including the windings, called the active part, is kept in a container often filled with dielectric liquid (Aasen 1995). A transformer consists of one or more phases that each have two windings, the primary where the current is coming in, and the secondary winding where the current is going out. The number of turns in the two windings is different depending on voltage ratio. The transformer is based on electromagnetic induction; when varying the current in the primary winding a varying magnetic flux in the transformer core is produced and by that a varying magnetic flux in the secondary winding is created. The variation in the magnetic flux induces a varying voltage in the secondary winding (Aasen 1995; M.Fishbane et al. 1996).

The insulation system in many high voltage transformers consist of dielectric liquid, often mineral oil and cellulose in form of paper and pressboard. The liquid function as coolant and electrical insulation while the cellulose function as electrical and mechanical insulation. The design of the insulating system in big transformer is a complex task.

During the power transformer life it suffers from stresses; thermal, electrical, mechanical and chemical which reduces the strength of the transformer all from the start. This reduces the: dielectric strength, mechanical strength, thermal integrity of circuit that carries the current and electromagnetic integrity. When the operating stresses are exceeded, a failure may occur and breakdown may follow. Electrical breakdowns in transformers are of major concern all over the world. Breakdown means that the voltage over the insulator gets too large and the critical electric field is exceeded leading to arcing and short circuits (Wilson 1980; Ding et al. 2009).

The stability in addition to the dielectric strength and the cooling properties of the dielectric liquids are very important. In transformer oil (mineral, vegetable and synthetic esters) oxidation of the liquids might be of the failure of largest concern. Resent also several failures of transformers all over the world can be linked to breakdowns likely caused by formation and deposition of conductive species (copper sulphide) in the paper insulation (Ding, Heywood et al. 2009).

The expected lifetime of the power equipment is an important parameter for the power suppliers and power equipment producers. It is therefore of a large interest to be able to predict the lifetime for the equipment and the material ageing, and find the best and most efficient way to produce equipment. It is also of interest to find possible methods for improving the equipment that already is in service.

The world population increases and the demand for and consumption of power increases and thereby the load in each transformer increases. Analyses of The Hartford Steam Boiler Inspection & Insurance Co of 78 business interruption losses between 1997 and 2001 show that the approximate cost was 9 $ per kVA (H.Bartley.P.E. 2003). The largest reported business interruption loss occurred in 2000 at a power plant and cost over 86 million $. The cause of these failures that has contributed to most breakdowns and highest cost is insulation failure, next are design, material or workmanship, and an unknown reason. Other reasons for failures include oil contamination, overload, fire and explosion, line surge, improper maintenance and operation, flood, loose connections, lightning and moisture. In total 94 cases of breakdown were counted in (H.Bartley.P.E. 2003) and the total cost was found to be near 300 million $. The average age of the transformers was 18 years at failure. (H.Bartley.P.E. 2003).

In the south of Norway (Kristiansand) a transformer failure occurred in July 2003 caused by formation of copper sulphide leading to flashover and breakdown (Figure 1). The transformer was repaired and in duty again in December 2003, in May 2005 the transformer failed and ended the life in October 2005. This was an extremely expensive (several billions Norwegian Kroner) breakdown due to the service cost and the range of application of the transformer (Ohnstad 2005; TU.no and Rudihagen 2006).

Figure 1. Picture of one phase from the transformer failure in Kristiansand 2005. The black areas in turn (copper windings) 87- 91 are caused by Copper Sulphide deposition in the paper. From (Ohnstad 2005).

1.2 Thesis outline

The work presented in this thesis is done as a part of a project financed by power suppliers and power technology industry and was performed at SINTEF Energy Research, Department of Power Technology in cooperation with The Norwegian University of Science and Technology (NTNU).

The thesis is divided into 8 parts giving an introduction, an overview of the theory of insulation, oxidation, corrosion and the methods used in this work, a summary of the papers included in this work, in addition to the conclusion of the work and future perspectives.

2 Insulating materials in transformers

High voltage (HV) transformer consists of a core of iron and insulated windings or groups of windings of conducting material, often copper (Figure 2). These windings have to be insulated to avoid electrical contact between the turns. In HV transformers the copper wires are insulated by oil-impregnated paper and pressboard (cellulose). In transformers with lower voltage esters, silicone oil and epoxy has been used lately, but for large HV transformers mainly mineral oil is used as dielectric material. In transformers heat is produced and high temperatures can damage the insulation. Therefore air cooling or oil cooling is used. Transformer oil has the characteristic property that it both cools down the windings and acts as an insulator between the windings. Due to varying temperatures over the transformer the oil circulates by convection so that the insulating liquid functions as a coolant and as a dielectric (Wilson 1980).

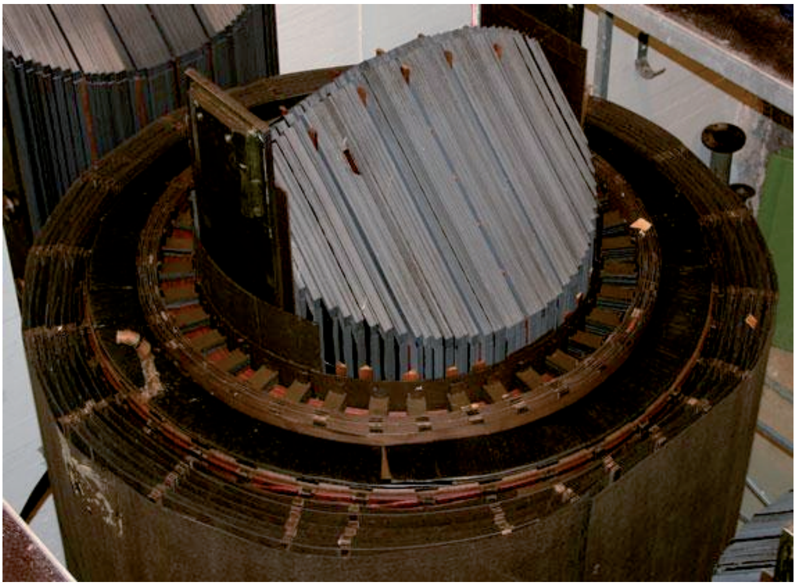

Figure 2. Picture of a phase from a transformer. The iron core of a transformer is shown in the middle (grey) with copper windings and paper around, from a post-mortem investigation. From (SINTEF 2012)

2.1 Liquids

Many transformers are filled with mineral oil, synthetic oil (silicone oil or synthetic ester) or natural esters (vegetable oils) as the dielectric liquid. These liquids have different properties with regard to stability and temperature influences.

An important parameter in the choice of insulating material is the flammability. Nearly all non-flammable liquids used in transformers have been halogenated hydrocarbons (chloro or bromo), for example the well-known persistent organic pollutant polychlorinated biphenyl (PCB). PCB is now banned by the Stockholm Convention on Persistent Organic Pollutant (SCPOP ; McShane 2001). Silicone based oils and fluorinated hydrocarbons are used where fire resistant liquids are required (indoor transformers etc.).

Millions of litres of oil are used in transformers all over the world, the risk of fluid spill are therefore of large concern. In addition to a low cost the ideal liquid should have good dielectric strength and low dielectric dissipation factor, the permittivity should be sufficient. High specific heat and high thermal conductivity is important. The gas absorption and the chemical stability should be high. Due to possible low temperatures in the working environment the low temperature flow must be good and the viscosity should be low. The liquid should ideally have a low flash point, be non-flammable, nontoxic, have low density, be cheap and available in addition to have good arc quenching properties. It is not possible to fulfil all these requirements, compromises and equipment design have to compensate for any shortcomings (Wilson 1980; Oommen et al. 1997).

Electrical and thermal stress causes degradation of the liquids and production of gas. These stresses are typically caused by poor design or failure during the construction of the equipment (Wilson 1980; Ding, Heywood et al. 2009). The most used liquids in transformers are flammable at higher temperatures and it is therefore important that the stability of the liquids is high to avoid arcing and breakdowns.

2.1.1 Mineral oil

As mentioned, mineral oils, refined from crude petroleum, are widely used in transformers as dielectrics and coolants. The composition of the crude oil originates from the reservoir it is extracted from. In addition to hydrocarbons the crude oil contains water, inorganic matter and gas; it is a very complex mixture. Crude oil is often classified as paraffinic, naphthenic (Figure 3), asphaltic and mixed (intermediate).

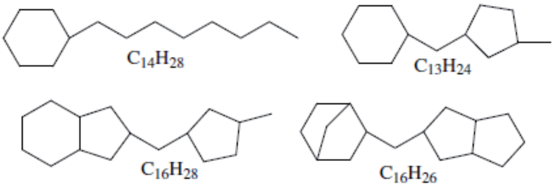

Figure 3. Naphthenic mineral oil molecules from (Liao et al. 2011)

Through refining processes of the crude oil; distilling, cracking, reforming and hydrorefining processes the oil products suitable for the different applications are produced, ranging from car fuel and plastics to transformer oils. During the refining processes waxes, sulphur, nitrogen and oxygen containing components are removed. When producing insulating oils, attention is paid to the electrical properties, oxidation stability and gas absorption properties (Wilson 1980).

The physical properties that are essential in the mineral oils are the thermal conductivity, the specific heat, coefficient of volume expansion, density, viscosity and pour point, but also the solvency, vapour pressure, and as mentioned flammability are essential. Important chemical properties are; the oxidation stability, gassing characteristic under electrical stress and under high temperature, neutralisation value (total acid number), saponification value, sulphur staining and corrosivity, nitrogen content, ionic contamination and water content. The electrical characteristics that are most important are; the electric strength, impulse strength, volume resistivity, dielectric dissipation factor and permittivity (Wilson 1980).

To improve the liquids the producers of dielectric liquids introduces additives to the oil that not normally are present in the petroleum. Antioxidants are widely used and gas absorbing additives have been used in dielectric liquids in HV cables. To avoid possible confusion with regard to the naming of the different additives, both natural and synthetic, the definitions valid in this text are;

- Antioxidants react with radicals and thereby interrupt the chain reaction and terminate the reaction.
- Deactivators react with the metal ions to prevent catalytical reactions with the metal. Chelates are formed with the metal ion and the deactivator.
- Metal passivators form a protecting film on the copper surface and protect the copper against corrosion.

More detailed description of these additives will be given later. The term inhibitor means chemicals that inhibit oxidation or corrosion. When discussing transformer oil; inhibited oil means oil added antioxidants (oxidation inhibitors). The concept retarder has also been used as a term describing antioxidants. In this text the terms will be used as mentioned; antioxidants, deactivators and passivators and inhibited oil (oil added antioxidants), and uninhibited oil (not added any antioxidants but may consist of natural antioxidants).

2.2 Esters as alternative insulating liquids

Petroleum products have an environmental risk; this includes also mineral oils used as insulating liquids and coolants. Mineral oils have poor biodegradability; this is also true for silicone oil and synthetic hydrocarbon fluids. Esters are a class of organic compounds made from organic acids and alcohols. Research has been done on the two main categories of esters; synthetic and natural esters (based on vegetable oils). Vegetable oils from plants as rape-seed and soya beans have demonstrated relatively good insulating properties and are biodegradable. Vegetable oil was among the insulating liquids that were first used in the manufacture of electrical machines (Clark 1962). From the 1990's researchers have studied the properties of vegetable oil as insulating liquids and coolants (Oommen 2002). Also synthetic esters (synthesised from raw products as petroleum) have been used as insulating liquids.

Crude vegetable oil from oil seeds have dark colour and are contaminated with proteins and fibres. The crude vegetable oil consists of fat and oil that are triglyceride esters of fatty acids. The fat consists of more saturated triglycerides and has a higher pour point temperature than the oils. Highly unsaturated oils are in liquid state down to -15 to -30^{o}C. (Oommen 2002). The oils have to be improved to be used in transformers, the purity of the oil is important, ionic impurities and other contaminants have to be removed from the oil. Separation of solid matter, bleaching and deodorizing are done to remove impurities. The conductivity should be below 1pS/m. The degree of unsaturation in the oil is an indicator of the thermal stability of the oil, the more unsaturated the more unstable oil (from mono to tri unsaturation). The content of mono-saturated glycerides should be over 80%.

The copper in the transformer increase the oxidation of the oils (Oommen, Claiborne et al. 1997). Oxidation inhibitors (antioxidants) have to be added to the oil to decrease the oxidation. The traditional antioxidants as 2,6 Ditert-butyl-p-cresol (DBPC) and food-grade antioxidants are not sufficient for use in the vegetable esters. The producers of the oils have composed special packages of complex phenols and amines. When large amounts of additives are used the conductivity is increased. To avoid oxidation sealed transformers are recommended for transformers filled with esters. Today there are two commercial vegetable products used as transformer liquids; BIOTEMP was patented in 1999 by ABB and was the first commercial product, Cooper introduces Enivrotemp FR3 to the marked in 2000. BIOTEMP and FR3 are reported to produce more CO_2 and CO than mineral oil, but are reported to prolong the life of the insulating paper. The vegetable oils are a mix of different esters that have different freezing points. This prevents formation of air pockets and cracks in the transformer (Oommen, Claiborne et al. 1997; Oommen 2002).

Synthetic esters are mainly polyesters and are suitable for use in transformers with regard to the dielectric properties and are more biodegradable than mineral oil. These esters have high cost but the low viscosity, high lubricity and low pour point have justified the use despite the cost. Synthetic esters have been used as PCB substitute in transformers since 1984 (Furlong et al. 2011).

2.3 Cellulose as insulating material

Cellulose has been important in the apparatus for generation, transmission and utilization of electric power for a long time. Cellulose is polysaccharides built of monomeric glucose units. As seen in Figure 4 the glucose units are linked together in very long chains. The linkages in cellulose are configurated so that the chains are linear and do not coil as many other glucose polymers. The linkage in cellulose is β-glycosidic linkages and presents a uniform distribution of –OH groups as seen in Figure 4. When cellulose chains get in contact the hydroxyl groups make hydrogen bonds and zip the chains together forming a highly insoluble, rigid and fibrous polymer. Cellulose is found as cell-walls in plants (Solomons and Fryhle 2000). The degree of polymerization (DP) gives the number of glucose units per chain.

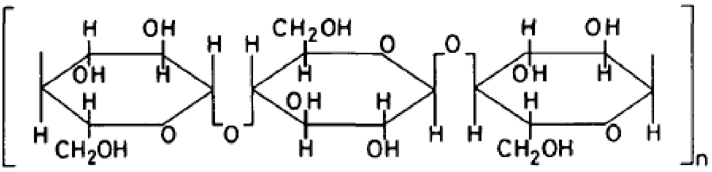

Figure 4. Glucose molecules in a chain, forming cellulose fibres (Shroff and Stannett 1985).

The combination of mineral oil and cellulose is used in many high voltage transformers as well as cables (Clark 1962). The cellulose has good dielectric properties but degradation during ageing can increase the conductivity and contribute to conductive contaminants in the oil. The DP normally starts in new transformers at 1200. By ageing the DP is reduced by chain cleavage. With decreasing DP the mechanical strength of the paper decreases. When the DP has reached 200 the paper has reached the end of life together with the transformer. The DP gives an indication of the remaining life of the paper in the transformer and is therefore an important parameter. The ageing is influenced by water content (hydrolysis), oxygen availability (oxidation) and temperature (Shroff and Stannett 1985; Lundgaard 2004).

Water (moisture) is an important factor in transformer insulations; the dielectric breakdown strength of both the liquid and the paper decreases with increasing concentration of water in the transformer. Moisture accelerates the ageing of paper, the water weakening the hydrogen bonds in the chains of glucose molecules (Lewand 2002).

3 Oxidation

Oxidation is when a chemical component (molecule or atom) donates an electron to another chemical component; this component is reduced by an increase in the amount of electrons. Often an oxidation is caused by oxygen transfer, where gain of oxygen means oxidation and loss of oxygen means reduction. Also hydrogen transfer is redox reactions, where loss of hydrogen is oxidation and gain of hydrogen is reduction, as the oxidation of alcohol to aldehyde, where hydrogen is removed.

In the literature, concerning mineral oil, oxidation means the chemical reaction between an oil molecule and oxygen and the following reactions caused by this initial reaction. These reactions involve hydrocarbon radicals, compounds with a free valence electron that easily reacts with hydrocarbons and further produce other radicals. Radicals are often denoted R•, where R is the hydrocarbon (Denisov and Afanas'ev 2005). The reaction mechanisms will be described more in the next part.

3.1 Oxidation mechanism in oil

The air contains 21 % oxygen (by volume) and is therefore of concern since oxygen is the main reason for oxidation of mineral oil in transformers. The solubility of oxygen at saturation is approximately 33000 ppm, while the normal dissolution of oxygen in free breathing transformers is low. It has been measured 2800 ppm oxygen in a 40 years old free breathing HV transformer (CIGRE in progress). As a rule; the organic compound is oxidized if the content of more electronegative elements than carbon is increased. Hydrocarbons react with oxygen to produce alcohols that further oxidize to aldehydes or ketones and water, further to carboxylic acids and finally to carbon dioxide;

Hydrocarbon → alcohol and hydrogenperoxide → aldehyde/ketone → carboxylic acid → carbon dioxide

The oxidation of the hydrocarbons is a complex chain reaction and goes through three main steps; initiation, propagation and termination. The rate of the oxidation is affected by the concentration of reactants, temperature and presence of accelerators (catalysts) or antioxidants (Clark 1962). In the initiation step a radical (R•) is generated when the hydrocarbon lose a hydrogen atom, this is a rare reaction that initiate the chain reaction (Wiklund and Biverstål 2009; CIGRE in progress). When the radical reacts with oxygen a peroxy-radical is formed. As long as oxygen is available this reaction can continue in a loop (propagation) as illustrated in Figure 5 and as the example in equation 2 and 3 below. The chain reaction is ended (termination) when the radicals react with each other so that the electrons are paired. The termination (the reactions listed below, 4-6) gives more stable products as alcohols, ketones, aldehydes and carboxylic acids (Fenske et al. 1941; Denisov and Afanas'ev 2005; Wiklund and Biverstål 2009). The oil is sensitive to light due to photo oxidation where light waves starts the oxidation processes by forming radicals (Lamarre and Crine 1985).

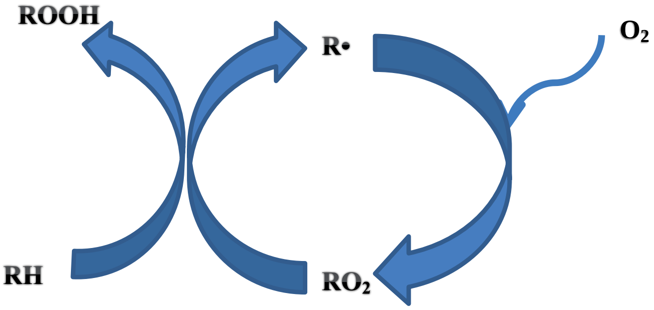

Figure 5. Illustration of the chain reactions in the oxidation of hydrocarbons. R denotes a hydrocarbon. (Denisov and Afanas'ev 2005).

Chain oxidation of hydrocarbons occurs by the following elementary steps where" I" denotes initiator, R is an alkyl:

$I \rightarrow R\bullet$ (endothermic) (1)
$R\bullet + O_2 \rightarrow RO_2\bullet$ (exothermic) (2)
$RO_2 + RH \rightarrow ROOH + R\bullet$ (exothermic) (3)
$R\bullet + R\bullet \rightarrow RR$ (exothermic) (4)
$R\bullet + RO_2\bullet \rightarrow ROOR$ (exothermic) (5)
$RO_2\bullet + RO_2\bullet \rightarrow$ Molecular products (exothermic) (6)

The heat produced by the oxidation is dependent on the structure of the oxidized group (Bolland and Gee 1946; Denisov and Afanas'ev 2005). In the temperature region from 140°C to 180°C the oxygen absorption doubles for each 10 degrees increase in the temperature (Fenske, Stevenson et al. 1941).

3.2 *Metals as oxidation catalysts*

Transition metal ions can react with ions, radicals or molecules in an electron transfer reaction (oxidation). These metal ions are oxidation catalysts and effective mediators in reactions involving electron transfer. The effect of catalysts is to increase the rate of reactions and is in the net reaction not consumed. Metal ions as catalysts in oil accelerate the oxidation of hydrocarbons and aldehydes by producing peroxides in reactions with molecules and decrease the temperature of the oxidation (Lee and Rungis 1996; Helbæk 1999).

The copper ions in the transformer oil origin from reactions between the hydroperoxide and the copper oxide surface, and from the reactions between free radicals with metallic copper (Lee and Rungis 1996) as in reaction 7:

$2RO\bullet + Cu \rightarrow Cu^{2+} + 2RO^{-}$ (7)

Catalysed oxidation can occur as reaction 8-9;

$$\mathrm{Cat} + O_2 \leftrightarrow \mathrm{Cat....}O_2 \xrightarrow{+RH} R\cdot \qquad (8)$$

$$\mathrm{Cat} + RH \leftrightarrow \mathrm{Cat....}RH \xrightarrow{+O_2} R\cdot$$

$$\mathrm{Cat} + RO_2\cdot \rightarrow \mathrm{Cat...}RO_2\cdot \rightarrow \begin{cases} \xrightarrow{+RH} P_s + R\bullet & (9a) \\ \text{Chain termination} & (9b) \end{cases}$$

Where Cat is the heterogeneous catalyst and P is the product. The RO_2• and R• are active radicals. The rate of oxidations increase with increasing concentration of catalyst, but this is not an unlimited increase; the oxidation rate reaches a maximum. The discontinuance of the catalytic reaction has been observed with an often very small increase in the concentration of catalyst. This is called the critical phenomenon. This phenomenon is caused by the nature of the chain mechanism of the oxidation and the ability of the catalyst to both initiate and terminate the reactions as seen in reaction (9a and 9b) This phenomenon has been reported in numerous observations and studies of catalytic oxidations (Kozlova et al. 1966; N.M.Emanuel and Gagarina 1966; A.Mukherjee and W.F.Graydon 1967; Neuburg et al. 1972; Varma and Graydon 1973; Srivastava and Srivastava 1975; Emanuel 1981; Denisov and Afanas'ev 2005; Temkin 2012). As seen in Figure 6, the absorption of oxygen increase with increasing amount of catalyst up to a certain point where the absorption of oxygen decreases with further increasing amount of catalyst.

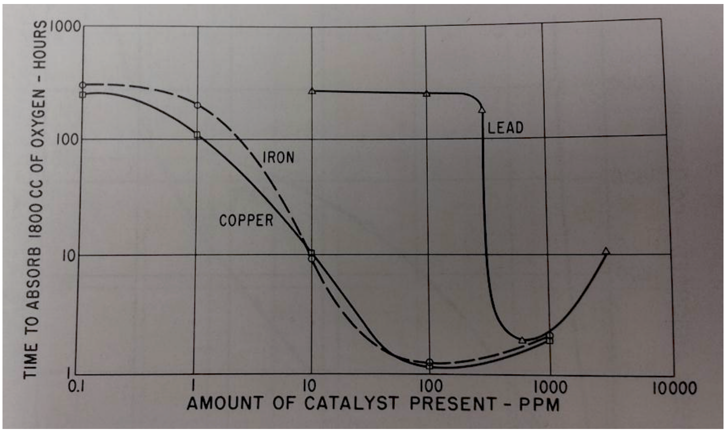

Figure 6. The effect of iron, copper and lead as catalysts on the time of absorption of oxygen in mineral oil at 150°C (the time to absorb 1800 cc for each 100 g oil) (Clark 1962).

The production of hydroperoxides in mineral oil increases in presence of copper, addition of metal deactivators reduce this formation of hydroperoxides (Melchiore and Mills 1965; Melchiore and Mills 1967). Deactivators react with the metal ions in the bulk solution (oil) preventing the ion from catalysing the oxidation reactions by stabilising the ion (Lee and Rungis 1996).

3.3 Antioxidants

Antioxidants have been used since the beginning of the 19th century and are used in many organic products from rubber to food, and in electrical insulations, both solid and liquid (Clark 1962; Denisov and Afanas'ev 2005). The oxidation and chain termination by antioxidants have been studied by several teams and the retarding action of antioxidants as phenols and aromatic amines were proven as a result of chain termination by the accepting of the peroxyl radicals.

There are three different ways the oxidation can be retarded;

- By breaking the chain reactions by acceptor reaction with peroxyl radicals.
- By breaking the chain reactions by use of an acceptor with alkyl radicals that reduces the oxidation.
- By introducing a chemical compound that decomposes hydrogen peroxide.

The chemical compounds that are used to inhibit oxidation of the dielectric liquids are antioxidants. The antioxidants can be divided into several different groups (Denisov and Afanas'ev 2005);

- Chain breakers that react with peroxyl radicals, forming intermediate radicals of low activity (reductive compounds with weak O-H and N-H bounds, phenols, naphthols, aromatic amines and diamines).
- Chain breakers that react with alkyl radicals (quinones, nitrones, iminoquinones, methylenequinones, stable nitroxyl radicals and nitro compounds that readily accept alkyl radicals).
- Antioxidants that decompose hydrogen peroxides without forming free radicals; sulphides, phosphides, arsenites, thiosulphates, carbamates and some metal complexes (chelating).
- Cyclic chain termination antioxidants. The antioxidants are regenerated in the chain termination reactions. The termination occurs as a catalytic cyclic process. Aromatic amines, nitroxyls radicals and variable valence metal compounds.
- Antioxidants of combined actions such as anthracene and methylenequinone can react with alkyl radicals and peroxyl radicals. Carbonates and thiophosphates can decompose hydroperoxides and break chains through the reaction with peroxyl radicals.
- The synergism of several antioxidants.

(Denisov and Afanas'ev 2005)

In transformer oil, two principles to achieve oxidation stability are used; naturally occurring antioxidants as sulphur species in the mineral oil (uninhibited oil) or highly refined oil added antioxidants (inhibited oil). In the inhibited oil the most used antioxidant is the phenol 2,6-di-tert-butyl-p-cresol also called 2,6 Ditert-butyl-p-cresol (DBPC) as shown in Figure 7 (Neto et al. 2004; Wiklund and Biverstål 2009).

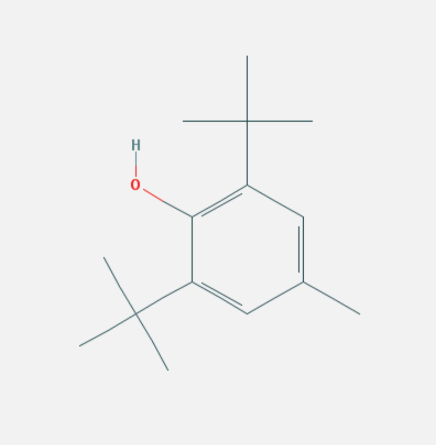

Figure 7. The molecular structure of DBPC (pubchem.ncbi.nlm.nih.gov).

Phenols or amine (InH) reacts fast with peroxyl radicals and terminate the chain reaction as in reaction 10-12 (Emanuel 1981; Denisov and Afanas'ev 2005);

$RO_2\bullet + InH \rightarrow ROOH + ArO\bullet$ (10)
$R\bullet + InH \rightarrow In\bullet + RH$ (11)
$ROOH + In\bullet \rightarrow InOOR$ (12)

Thise reactions are exothermic (Denisov and Afanas'ev 2005). The phenoxyl radical (ArO•) react with another radical and thereby quench the chain reactions (Wiklund and Biverstål 2009). The phenoxylradical can also react with dioxygen and form a quinolide peroxide (ArOO•) that will react fast with a phenoxyl radical and quench the start of a chain reaction (Denisov and Afanas'ev 2005).

In the uninhibited oil, sulphur species reduce the hydrogen peroxides to alcohol and by that stop the chain reaction. The sulphur species may be corrosive to copper so there has to be a balance between the effect of oxidative stability and the corrosion properties. Naturally occurring sulphur species in uninhibited oils are antioxidants due to their effect of sulfoxidation of hydrocarbons. By reaction with radicals the sulphur species form stable sulphur products and thereby ends the chain propagation as seen in reaction 13, sulphur species can act as inhibitors (>SH) where P is a product(Emanuel 1981; Denisov and Afanas'ev 2005);

$ROOH + {>}SH \rightarrow P$ (13)

Sulphur species can also poisoning the catalytical sites on the copper surface (Bartholomew 2001).

As mentioned, the copper ions function as catalyst in oxidation process of hydrocarbon solutions. Deactivators are therefore used in transformer oils, these deactivators are ligands that binds to the copper ions in the solution and thereby deactivates the copper. Bi-dentates as disalicylidenethylenediamine are used. The copper ion binds to the ligand both to the oxygen in the hydroxyl groups and the nitrogen, forming a five-membered ring with copper in the middle (chelating).

Synergism between antioxidants and metal-deactivators increase the oxidation stability of the oil in transformers (Krishnamoorthy et al. 1992). Also Neto et.al. have shown that the combined effect of the antioxidants and metal passivator is larger than the individual effects with regard to oxidation (Neto, Lima et al. 2004).

4 Corrosion

Corrosion gradually destructs a material, often metals, by chemical reactions with the environment. A well-known example is the green colour of copper, verdigris, or copper rust (this is also an oxidation, where the copper is oxidised).

When a metal corrodes, an electrochemical reaction occurs where electrons leaves the metal atom (oxidizes), the metal is an electron donor. The electron acceptors are often an acid, oxygen, carbon dioxide (acid) or sulphur-specie and cause the corrosion.

In transformers (even young) the formation of sulphide deposition on the copper surface and the paper have caused failures due to conductive copper sulphide leading to flashover through the paper. In 2009 a CIGRE working group estimated that about 100 failures in transformers were caused by copper sulphide (Atanasova-Hölein 2009; CIGRE 2009). About 50% of the transformers installed after 1990 have tested positive on corrosive sulphur (Scatiggio et al. 2009). In Figure 8 the change in concentration of sulphur in produced mineral oil in the time between 1964 and 2008 used in transformers is illustrated.

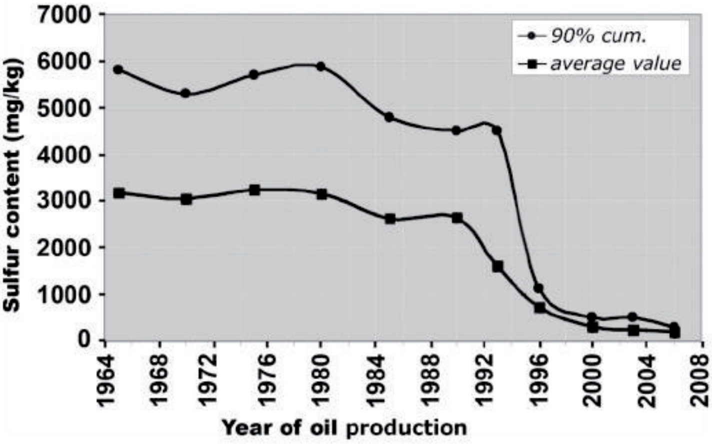

Figure 8. The total sulphur content in mineral oil produced for use in transformers and shunt rectors between 1964 and 2008 (Scatiggio, Tumiatti et al. 2009).

4.1 Copper sulphide in transformer windings

As mentioned in the past chapter sulphur containing components are good antioxidants in mineral oil, and natural inhibited oils contain sulphur components as antioxidants. Highly refined oils do not contain sulphur and do not have the natural inhibition from the sulphur components and antioxidants are added. Although sulphur components may function as antioxidants in the transformer oil, the sulphur has been a major concern since the beginning of this millennium due to the formation of copper sulphide on the transformer windings leading to a conductive bond through the paper insulation on the copper winding and thereby leading to a breakdown (Figure 9).

Figure 9. Picture of a part of a copper winding with paper from the transformer breakdown described in Chapter 1. From (Ohnstad 2005).

The mechanism of these formations is not well known, but there is presented a model suggesting that the copper sulphide is formed and deposited on the paper in a three-step mechanism (illustrated in Figure 10);

- Dissolution of DBDS-Cu into the insulating liquid.
- Absorption of DBDS-Cu on the paper.
- Decomposition of DBDS-Cu on the paper.

(Kawarai et al. 2009) (Bengtsson et al. 2005)

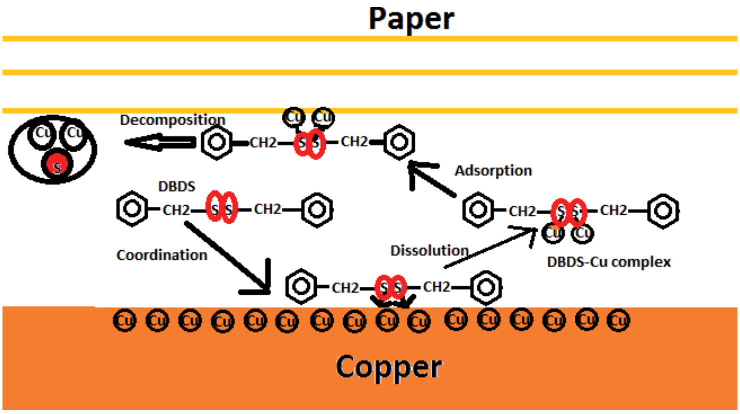

Figure 10. Illustration of the formation of copper sulphide on paper and copper (CIGRE 2009).

When the copper surface is covered with an oxide layer the reaction can be written as in reactions 14 and 15 (Ren et al. 2009):

$Cu_2O + 2RSH \rightarrow 2CuSR + H_2O$ (14)

$2CuSR \rightarrow Cu_2S + RSR$ (15)

By corrosive sulphur in transformer oil, means sulphur that is corrosive at the operating temperatures of the transformer. The corrosivity of the sulphur is dependent on the type of oil; paraffinic oils gives less corrosive effect of sulphur than naphthenic oil (Scatiggio et al. 2008). The corrosivity of sulphur species are varying from elemental sulphur and mercaptans (thiols) which are very reactive, sulphides are reactive, disulphides are less reactive and thiophenes are very stable (Lewand 2002; Desai 2006; Lewand 2008). Dibenzyl disulphide (DBDS) has been recognised as an important copper sulphide forming agent (Atanasova-Hölein 2009).

The electrical properties of the oil impregnated paper in transformers are changed by copper sulphide. The dissipation factor (tan d) and resistivity are increased. Contamination of the paper is a thermally activated chemical reaction; the contamination increases with increasing temperature in the transformer. The hottest parts of the transformer have the most contaminated paper windings. To decrease the effect of corrosive sulphur in the oil, metal passivators are added to the oil (Scatiggio, Tumiatti et al. 2008; CIGRE 2009).

4.2 Passivators and deactivators

Metal passivators are used in transformer oils to prevent reactive compounds from reaching the metal surface. Metal passivators, in addition to antioxidants and deactivators, decrease the oxidation of oil (Neto, Lima et al. 2004).

One of the most used metal passivator in transformer oil is Irgamet39^{TM} (from Ciba, I39, Figure 11). This passivator is based on tolytriazole (TTA) (Figure 12) a benzotriazole (BTA, Figure 11) with a methyl group, which is made more oleophilic with a methylamine “tail” as seen in Figure 11. The chemical nomenclature of two isomers of I39 is N,N-bis(2-ethylesil)-4-methyl-1H-benzotriazol-1-methylammine and N,N-bis(2- ethylesil)-5-methyl-1H-benzotriazol-1-methylammine (CIGRE).

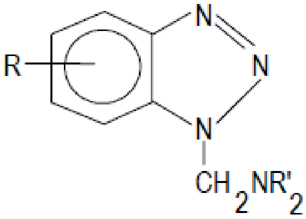

Figure 11. The molecular structure of Irgamet 39 (Ciba 2005).

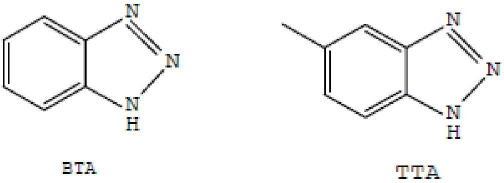

Figure 12. The molecular structure of benzotriazole (BTA) and tolytriazole (TTA)(Wan et al. 2012).

The I39 forms a thermally protecting film on the copper surface. The I39 loses the methylamine "tail" when adsorbing on the copper surface. This leads to a TTA molecule on the copper surface (Levin et al. 2007; Wiklund 2007; Wiklund et al. 2007).

Many studies are reported in the literature on how BTA behaves in solutions and on surfaces. Cotton and Scholes postulated in 1967 that BTA forms a polymeric linear structure on the surface as seen in Figure 13. This has been supported by several other studies (Dugdale and Cotton 1963; Cotton and Scholes 1967; Poling 1970; Sease 1978; Rubim et al. 1983; Lewand 2006; Finšgar and Milošev 2010). With improved measuring techniques (e.g. surface tunneling microscopy and atomic force microscopy) several researchers have lately found that the BTA probably is oriented vertically on the surface or with a tilt (e.g. Figure 14), but this is still discussed (Fang et al. 1986; Walsh et al. 1998; Cao et al. 2002; Jiang and Adams 2003; Lewand 2006; Finšgar and Milošev 2010).

I39 acts as both a passivator and a deactivator where the I39 forms a film on the copper surface and forms complexes with copper ions in the oil (Lee and Rungis 1996; Lewand 2006).

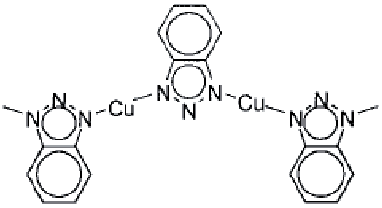

Figure 13. The suggestion of the formation of copper-BTA film on the copper surface (Cao, Yao et al. 2002).

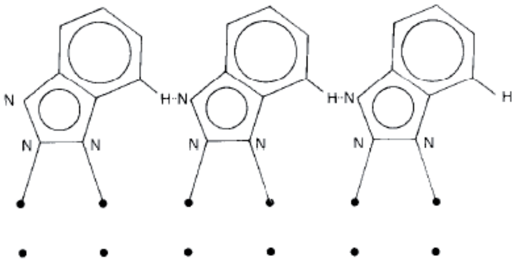

Figure 14. Proposed structure of the chemisorption of BTA on Cu, proposed by Fang, Olson et.al. (Fang, Olson et al. 1986).

5 Methods and experiments

Classic and new analytical methods have been used in this work. The main methods have been isothermal microcalorimetry and potentiometric titration in addition to crystal quartz microbalance (QCM) and UV-Vis spectrophotometry. These methods will be briefly described and the reason for the selected method will be given. The experiments can be divided into two main parts; oxidation stability testing and studies of a metal passivator.

5.1 Oxidation stability studies

Oxidation stability in dielectrics is an important factor in the transformer performance. Accelerated ageing tests by different methods have been performed for several decades. One traditional method on study of oxidative stability of dielectrics is the bottle experiments where the ageing of the oil is accelerated by heating the oil in bottles and the changes in parameters such as total acid number (TAN), water content and sludge are measured over time (Lundgaard 2004; Lundgaard et al. 2005; CIGRE in progress).

Several standard tests that are often used in determination of the oxidation stability are tests based on ageing of oil at high temperature and oxygen flow (IEC 61125 and ASTM D2440, Table 1 section 5.1.1). Rotary Pressure Vessel Oxidation Test (RPVOT, ASTM D2114, Table 1) are based on the measuring time until the oxygen pressure has reached a certain value (the oxygen consumption). In turbine oxidation stability test (TOST) an oxygen flow (controlled) is purged through a mixture of water, oil, copper and iron catalysts at 95^{o}C until the acid number reaches 2.0 mg KOH/ g, the results are given in hours (Pach et al. 2006). Common features for these methods are the extreme conditions the oil is exposed to compared to those found in an actual transformer. Pressure differential scanning calorimeter (PDSC, Table 1, section 5.1.1) is also a method used for oxidation stability testing. PDSC is a method where the temperature is programmed to increase with a particular (linear) rate and the heat flow is measured against the temperature rise. All these methods mentioned here are rough methods to the samples. Many of these methods are also relatively time consuming; the bottle experiments may be performed over years, for inhibited oil the IEC 61125 takes 500 h.

5.1.1 Microcalorimeter for studying oxidative stability

Calorimetry is a method for measuring the heat formation, the rate of heat formation and the heat capacity of a sample. Chemical reactions and physical processes produce or consume heat; this heat can be measured and gives a measure of the process or reaction as; oxidation reactions, ligand bonding, adsorption or desorption on surfaces. Isothermal microcalorimetry is used in many different areas such as food industry, pharmaceutical industry, development of propellants and now lately in the research on insulating materials in transformers (Forsström 1999; Roškar et al. 2007; Liland 2008).

An isothermal microcalorimeter has earlier been used in investigation of the oxidation stability of polymers and the effect of inhibitors in polymers (Forsström 1999). Oxidation of cellulose has also been studied by means of an isothermal microcalorimeter (Liland 2008; Ese et al. 2010). In this work an isothermal microcalorimeter has been used to study the oxidation stability of hydrocarbons.

Equation 5.1 gives the energy balance for the calorimetric cell (Thermometric 2004);

$$\frac{dQ}{dt} = \Phi + C\frac{dT}{dt} \tag{5.1}$$

Where dQ/dt is the rate of heat production by the sample, Φ is the exchange of heat from the system to the surroundings, C is the heat capacity of the sample and dT is the change in temperature during the time dt (Wadsö and Goldberg 2001; Thermometric 2004).

The idea of using a microcalorimeter was to lower the time of testing and to try a more gentle method without purging the sample with oxygen. An opportunity came up with a CIGRE' Round Robin testing programme with the working group; Oxidation stability of transformer liquids (under the study committee Materials and Emerging Test Techniques, D1.30) where several member laboratories received a set of unknown samples as listed in Table I in the appendix A (U1-U16). CIGRE' is the "Council on Large Electric Systems" and was founded in 1921 as a non-profit association for promoting collaboration between experts worldwide and sharing knowledge and joining forces to improve electric power system (CIGRE 26.11.2012). This Round Robin test made it possible to study the microcalorimetry method with regard to oxidation stability of dielectrics and compare the results with other methods used for oxidation stability testing listed in Table 1.

Table 1. Overview of the methods used in the CIGRE' Round Robin testing programme (Hoehlein and Wiklund ; CIGRE in progress).

Method	Time	Temp. (^{o}C)	Gas and gas flow	Parameter measured
IEC 61125 C induction time	165 h-500 h	120	Air, 0.15l/h	TAN, Sludge, Dielectric dissipation factor (DDF)
RPVOT (Rbot ASTM D2112)	Meas. min. to ΔP=175kPa , induction	140	Oxygen, (100rpm 620kPa)	Time, Gas formation
PDSC	Onset time (min)			Temperature, Heat formation
Isothermal microcalorimeter	45h/350h	110/ 90	Air, ampoule	µW/g*h

The microcalorimeter was shown to be well suited for the determination of the oxidation stability of the dielectrics. The results of the oxidation determination of the unknown samples are published in Paper I.

The capacity of the microcalorimeter in determination of the oxidation stability were followed up by studying the effect of additives in liquid hydrocarbons and esters with regard to the oxidation stability, these results are presented in Paper II.

5.1.2 Experiments with isothermal microcalorimeter

An isothermal microcalorimeter was used to investigate the oxidation stability of dielectric liquids and to investigate the effect of different additives in hydrocarbons; copper, DBDS and Irgamet39 (I39). All the samples are presented in Appendix A.

The isothermal microcalorimeter was a TAM III from TA Instruments. The module of TAM III used in this work has four calorimeters; nanocalorimeter, minicalorimeter (4 ml), microcalorimeter (20 ml) and macrocalorimeter. The thermostat specifications for the used microcalorimeter are given in Table 2 (TAinstruments).

Table 2 Thermostat specifications (TAinstruments).

Thermal media	oil
Temperature range	15- 150^{o}C
Accuracy	< ± 0,1 ^{o}C
Long term stability	<±100 µK/24 h
Short term stability	<± 10µK (p-p)

20 ml steel ampoules were used in this work with the precision of the microcalorimeter is ± 100 nW and the accuracy 2% (TAinstruments).

The liquids used in the experiments are given in Table I in appendix A. Most experiments were performed at 110^{o}C but some experiments were performed at 120^{o}C and 90^{o}C. To avoid any contribution to the signals caused by possible interactions between I39 and the surface of the steel ampoules, glass cups were inserted in the ampoules. All this information is included in appendix A. To remove air from the sample, the liquid was purged with nitrogen in some experiments. The procedure of the experiments is described in Paper I and II.

5.1.2.1 Handling the results from isothermal microcalorimeter

The microcalorimeter consists (in addition to the main apparatus) of a computer with software (TAM assistant) that both have a stepwise guide to perform the experiments and tools to manage the results. The curves are displayed and the data can be exported to a spread sheet for further treatment (Microsoft, Excel) by the TAM assistant software. The data from the experiments was exported to Excel and treated there before exported to SigmaPlot (Systat Software Inc.) where the graphs were plotted and the area below the curves were determined by numerical integration.

An important part of the data treatment is the baseline subtraction. The calorimeter contains an empty ampoule that records the signals for the baseline. This baseline can be subtracted from the sample signals. The subtraction is done with the TAM Assistant software prior to the export to the spread sheet.

5.2 Adsorption and the effect of passivator on copper

As explained in chapter 4.2, passivators are added to transformer oils to protect the copper surface from corrosion. In experiments reported by other researchers a large range of methods have been performed to study the adsorption of BTA as mentioned in 4.2, these include electrochemical methods, elipsometry, chromatography (Wiklund 2007), spectrometric methods as x-ray photoelectron spectroscopy, Auger electron spectrometry and IR spectrometry (Poling 1970) have also been used. Surface analysing methods e.g. surface Enhanced Raman Scattering (Rubim, Gutz et al. 1983), atomic force microscopy and scanning tunnelling microscopy have been applied (Finšgar and Milošev 2010). Theoretical calculations have also been performed to investigate how BTA probably adsorbs on copper (Jiang and Adams 2003). In this research traditional methods such as titration and spectrophotometry in addition to a new method in this field, Quartz crystal microbalance (QCM) have been used.

I39 forms a protecting film on the copper surface. It was therefore desirable to study in greater detail the adsorption of I39 on copper. In addition ageing experiments were performed with copper in mineral oil in sealed head space vials, as well as determination of the effect of I39 by titration and visual inspections.

5.2.1 Quartz crystal microbalance (QCM) sensor

The Quartz crystal microbalance (QCM) is a mass selective sensor using a thin quartz crystal covered with electrode plates. The crystal is piezoelectric; by applying an oscillating electric field over the QCM an acoustic wave is induced through the crystal. The idea was that the QCM could give the possibility of studying the weight change due to adsorption of I39 on copper.

The resonance caused by the applied electrical field will change with change in the mass. The change in frequency can be interpreted as change in the mass on the crystal surface per area (O'Sullivan and Guilbault 1999). Sauerbrey showed that the shift in the resonance frequency is linearly dependent on the adsorbed mass on the crystal surface as in equation 5.2.

$$\Delta m = \frac{C\Delta F}{n} \qquad (5.2)$$

C is the Sauerbrey constant, Δm is the mass change, n is the overtone and ΔF is the frequency change (Sauerbrey 1959). When the frequency change is constant, the adsorption has reached equilibrium and the total mass adsorbed on the surface is obtained. The frequency shift from the baseline to this value is the delta frequency (ΔF) change used in the equation 5.2. An overtone is a multiple of the fundamental frequency, each overtone penetrates the substance on the crystal with different depths (Alonso and Finn 1992; q-sense 2006).

Another method of obtaining information from the QCM measurements is a Dissipation-frequency plot (D-F plot, Figure 15). By plotting the change of dissipation energy (ΔD) versus the frequency change (ΔF), induced energy loss per coupled unit mass can be calculated. The dissipation energy is the energy lost to the environment from the crystal; a large ΔD value indicates a viscoelastic layer due to energy lost, and this could either be multiple layers or a very large and flexible molecule (Marx 2003).

As illustrated in Figure 16 a rigid layer (A) give a low dissipation value (D_A), a monolayer with a low rigidity as B_1 have a dissipation value (D_B) larger than D_A. Also the formation of multilayers gives a less rigid layer (B_2) and the dissipation value becomes larger.

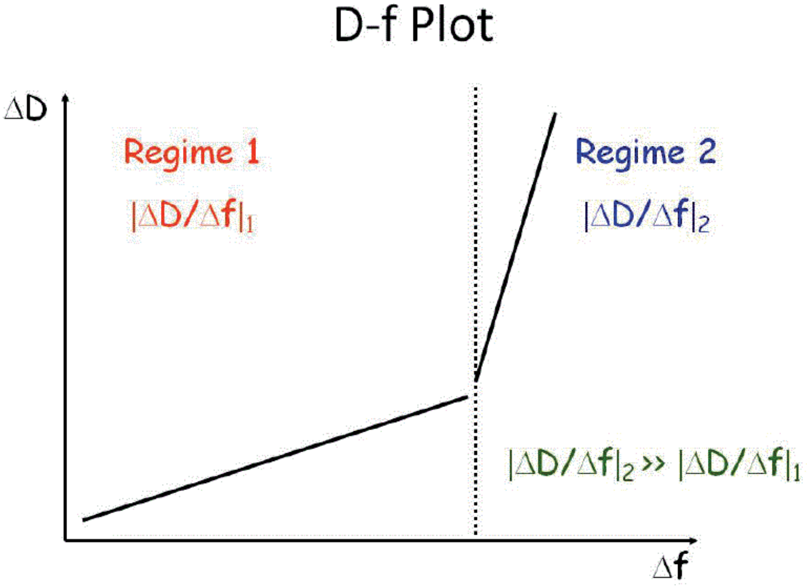

Figure 15. Illustration of D-F plot. ΔD gives the change of dissipation and Δf gives the change in the frequency caused by change in mass on the crystal (Roel 2010).

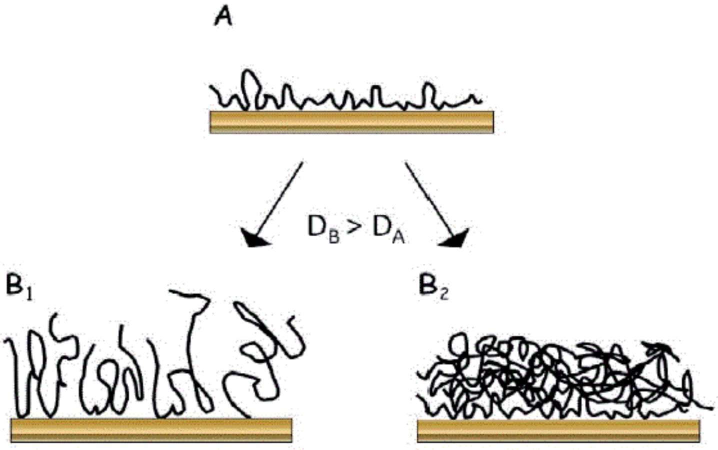

Figure 16. An illustration of different orientations and layer configurations. In the upper figure (A) it is demonstrated a small rigid layer, in the figure down to left (B_1) the added mass has a low rigidity (floppy) and in the figure down to left (B_2) the molecules forms a multilayer (Roel 2010).

5.2.2 Experiments with QCM

The experiments done with the QCM were performed with a KSV QCM Z500 from KSV instruments ltd and the crystal was a QSX 313 Sensor Crystal CU 5MHZ quartz crystals (Roel 2010).

The procedure is described in Paper III. Due to the viscosity of mineral oil, heptane and toluene were used as model oils. The I39 was diluted to a concentration of 100 mg/kg and added to chamber with the QCM disc seen in Figure 17.

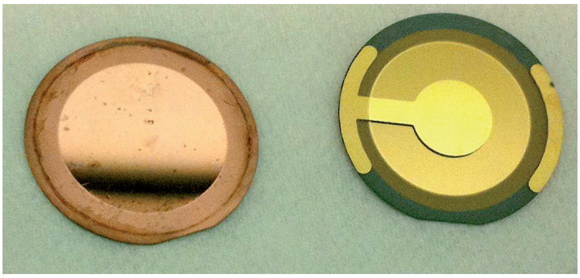

Figure 17. Crystal Quartz Microbalance sensor covered with Copper from q-sense. The left disk shows the copper surface. Photo: Marius Roel (Roel 2010).

The signals from the QCM measurements are the change in frequency caused by the change in mass on the surface of the QCM-crystal. The Δf (equation 5.3) is plotted against the time as demonstrated in Figure 18 where the first plateau (1) is the baseline, the frequency of the solvent and used as the reference for this experiment.

$$\Delta f = f_{start} - f \qquad (5.3)$$

The time used to achieve the baseline is short compared to the time of the rest of the experiment so the baseline is hardly visible in the plots of the experiments. The first break (2) in the frequency change vs. time plot is the addition of the sample. Next plateau (3) is the initial layer or monolayer. (4) Is assumed to be where the monolayer coverage is completed. After point 4 (more to the right) the overtones diverge, indicating multilayer being formed, leading to inaccuracy when using the Sauerbrey equation (5.2).

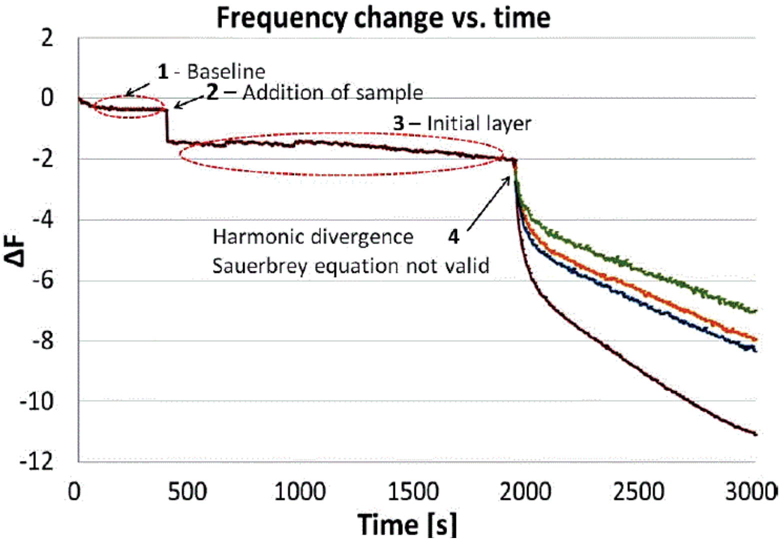

Figure 18. Delta frequency change vs. time plot illustration of the different physical characteristics of QCM adsorption (Roel 2010).

5.2.3 Spectrophotometer

To measure the change in the I39 concentration in a liquid ultraviolet –visible (UV-Vis) spectrophotometer is well suited. The spectrophotometry is based on the absorbance of electromagnetic radiation (UV-Vis in this case). A molecule absorbs light at a specific wavelength, as long as there are no interferences caused by other molecules that absorb a light in wavelengths close to that of the measured molecule the method provides good selectivity.

In UV-Vis spectrophotometry an UV-Vis light is sent through a sample (transmitted), the difference between the light before the sample and after the sample is measured. The absorbance (A) of the solution can be written as the negative logarithm of the transmittance as seen in equation 5.4

$$A = -\log T = \frac{P_0}{P} \qquad (5.4)$$

Where T is the transmittance, P_o is the incoming radiation and P is the outgoing radiation. This is called Beer-Lambert law (or also known as Beer’s law)(Skoog et al. 2004). By using a calibration curve the concentration of the sample is found by comparing the absorbance with this curve.

5.2.4 Experiments with UV-Vis spectrophotometer

The UV-Vis spectrophotometer used in this work was a Shimadzu UV-2401 PC with a quartz cuvette from Hellma with light in the wavelength region 200 – 600 nm. The samples were measured at room temperature (Roel 2010).

To study the rate and amount of adsorbed I39 on copper, samples with white mineral oil (described in appendix A, Table I) were aged at 80^{o}C and 90^{o}C with I39 and copper coupons in sealed head space vials. Samples were sampled at decided times from 1 hour to 72 hours and the concentration of I39 in the oil was measured with the spectrophotometer. These experiments are described in Paper III.

5.2.5 Copper strips experiments with passivator and corrosive sulphur

A much used method to study the corrosivity of a dielectric liquid involves copper or silver strips wrapped with paper in oil at high temperature (150^{o}C) over a period of time. The copper and paper are then analysed visually and compared to a standard to determinate the corrosivity of the oil (CIGRE 2009).

In this work copper pieces wrapped with paper from unused transformer windings were used. The copper and paper were aged at 150^{o}C for different time intervals and under varying oil conditions. The primary purpose for the experiments was to investigate the effect of the passivator in aged oil and the effect of the passivator if the copper already had started to corrode. *Will the passivator be effective towards corrosion when added after copper-sulphide corrosion has been initiated in transformers?*

After the ageing of the samples was ended, the total acid number and the concentration of free sulphide species were measured with potentiometric titration. The copper and paper were also studied visually by comparing the appearance of depositions with reference samples.

5.2.5.1 Potentiometric titration

Potentiometric titration was used for measuring the concentration of sulphur species and the total acid number. The method combines the selectivity of potentiometry with the sensitivity of titration.

In potentiometry the potential between two electrodes are measured and from Gibbs law equation 5.5 can be derived (for a liquid filled electrode).

$$\Delta G = \Delta H - T\Delta S = -\mathrm{RT}\ln\left(\frac{a_{i,sample}}{a_{i,int.soln}}\right) \qquad (5.5)$$

ΔG is Gibbs energy, ΔH is the change of enthalpy, T the temperature, ΔS the change of entropy, R the universal gas constant (8,134 J/Kmol), $a_{i,\ sample}$ is the activity of the sample and $a_{i,int.soln}$ is the activity of the intern solution in the electrode.

The free energy difference will then be as equation 5.6 and gives the corresponding potential produced across the membrane.

$$E = -\frac{\Delta G}{nF} = \frac{RT}{nF}\ln\left(\frac{a_{i,sample}}{a_{i,int.soln}}\right) \qquad (5.6)$$

Where E is the free energy, F is Faradays constant, n is the number of electrons transferred. The activity in the inner solution and n are constant and can be baked into a constant K. The cell potential of an ion-selective electrode can then be written as equation 5.7

$$E = K + \left(2{,}303\frac{RT}{z_i F}\right)\log a_i \qquad (5.7)$$

z_i is the charge and a_i is the activity of the ion. By measuring the potential (E) over the membrane a_i is found. A much used approximation is that $a_i \approx$ the concentration of the ion. By this approximation as an example the potential of a standard pH electrode can be written as equation 5.8 also known as the Nernstian potential

$$E_{cell} == K + 0{,}059pH \qquad (5.8)$$

Potentiometry is used in a wide range of fields, ranging from sensors during surgical intervention, industrial process controls to environmental monitoring. The potentiometric methods are fast cheap and accurate (Wang 2000).

The combination of the accuracy of titration with the selectivity of potentiometry provides a good method to measure the concentration of acids and sulphur.

5.2.5.2 Acids in transformer oils

As mentioned in chapter 3 acids are some of the end products caused by oxidation of the oil. Acids corrode the metal and damage the paper in the transformers. Measurements of the total acid number (TAN) have for a long time been a much used measure of the oxidative state of the oil (Solomons and Fryhle 2000; Denisov and Afanas'ev 2005; Wiklund and Biverstål 2009; Pahlavanpour et al. 2010). It was therefore interesting to look at how the corrosion on copper and the passivator in the oil affect the TAN. The TAN was measured in this work using potentiometric titration. The electrode used in these experiments was a glass-electrode for non-aqueous media (Solvotrode from Metrohm).

The oil-sample was diluted in 2-propanol and titrated with potassium hydroxyl in ethanol (KOH in EtOH). The change in the acidity was registered with the glass-electrode as described in 5.2.5.1. More details are published in Paper III.

5.2.5.3 Sulphur species in transformer oil

When corrosive sulphide species reacts with copper the amount of free sulphide species in the oil will decrease corresponding to these reactions. By measuring the concentration of free sulphur species in the oil, the amount of sulphur that has reacted with copper can be presumed to be the same amount as the change in concentration from the start concentration of free sulphur species.

The concentration of thiols and disulphides (sulphur species) in the oil samples was measured by potentiometric titration using a combined Ag ring electrode (Metrohm), with silver nitrate as titrant. For standardization of the $AgNO_3$ solution octadecylmercaptane in white mineral oil with acetic acid (100 µL) was used. Zinc was used for the reduction of disulphide to thiols according to reaction 16 (Karchmer and Walker 1958).

$$Zn + RSSR + 2H^{+} \rightarrow 2RSH + Zn^{2+} \qquad (16)$$

More details are presented in Paper III.

6 Presentation of papers included in this thesis

The scope of this doctoral work has been to focus on corrosion and formation of copper sulphide in transformers and oxidation of insulating liquids in transformers.

To investigate oxidation of insulating liquids, known as a large problem in transformers, an isothermal microcalorimeter was used. Mineral oils, a vegetable ester and hexadecane were used in this study (Paper I and II).

The metal passivator Irgamet39 (I39) was studied to investigate the effect on already corroded copper and to study the adsorption of I39 on copper (Paper III). It was seen that the effect of I39 can be weakened of oxidation products in the insulating liquid, this was investigated both with traditional methods as potential titration and with an isothermal microcalorimeter. The I39 is used in transformers as passivator and deactivator, the effect; regard to oxidation, from this passivator is studied in the microcalorimeter (Paper II).

6.1 Paper I and Paper II

Oxidation is an important reason for failures in high voltage transformers. It is therefore important to recognize the mechanism of the oxidation and also have methods to determine the stability of dielectrics used in transformers with regard to oxidation. Ageing of the dielectrics by heating and applying oxygen has been a much used method. This is time consuming and very rough regard to oxygen and temperature conditions and it is therefore of interest to develop faster and cheaper methods to identify the oxidative stability of the dielectrics.

The apparatus used in these two papers is the isothermal microcalorimeter as described in chapter 5.1. One of the problems with the calorimetric measurements is the fact that it is the total amount of heat produced and consumed in the reactions that is measured; calorimetry is a non-specific method. The heat flow is a result of the total amount of reactions in the system. In the beginning of the experiments it is difficult to know if the heat flow is caused by the temperature adjustment in the calorimeter or the reactions in the sample system. As seen in Figure 19 the signals in the beginning appear to be interfered by the temperature adjustments.

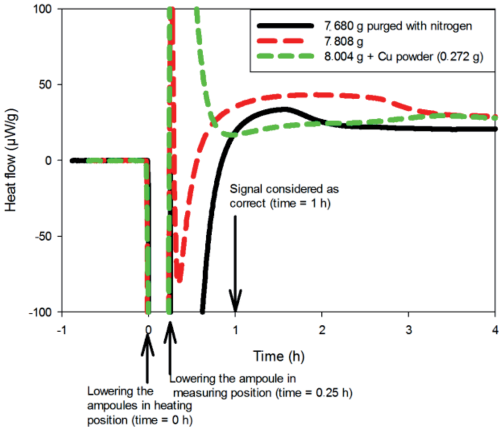

Figure 19. Initial part of the microcalorimeter curves (heat flow vs. time) with no baseline correction for hexadecane with (green dashed line) and without copper powder (red dashed line) and purged with nitrogen (black line).

6.1.1 Paper I: Isothermal microcalorimetry as a tool for studying oxidation stability of insulating liquids

To investigate if the isothermal microcalorimeter can be used for determine the oxidative stability of dielectric liquids a set of known oils; uninhibited, inhibited, base oil and white mineral oil were heated in the microcalorimeter and the heat flow was registered. It was found that for a given oil, the area below the calorimeter curves correspond to the ratio between the volume of oil and volume of the air above the oil in the ampoule used for analysis. The area is illustrated in Figure 20.

For both the base oil (Figure 21) and the uninhibited oil the peaks appear at approximately the same time for all the samples. The area under the curves decreases with increasing ratio of the volume of oil over the volume of air above the oil (head space), showing that the oxygen present in the gas volume contributes to the oxidation reactions (Figure 21). Also the height of the peaks is larger for lower oil/air ratios. Because of the correction of the signal with regard to the weight (normalization) we assume that the signal observed in the calorimeter is mainly caused by oxidation reactions.

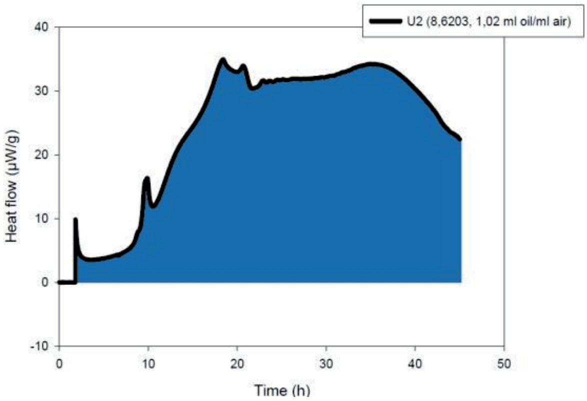

Figure 20. Example of microcalorimetry curve. (Oil: Unknown sample 2 in the presence of air, ratio oil : air = 1.02 ml/ml).

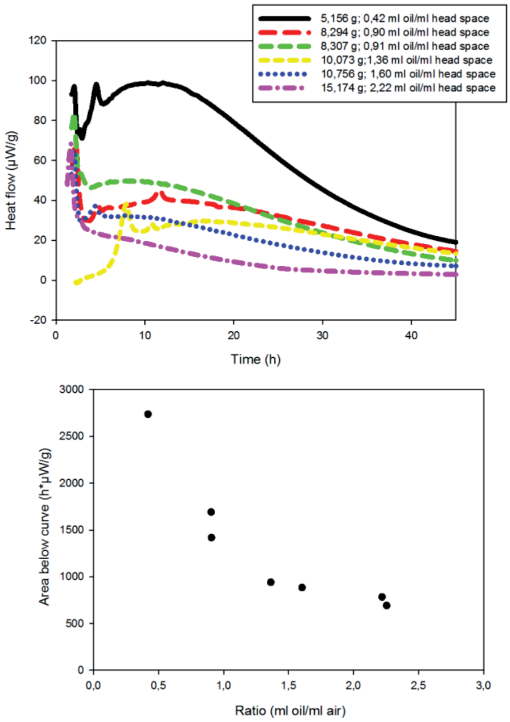

Figure 21. Illustration of the effect of varying volumes of air in the ampoule. Upper: Microcalorimeter curves (heat flow vs. time) for base oil with different ratios between oil and air. The baseline is subtracted. Bottom: The area below the curves (h*µW/g) for the different volumes of base oil in 20 ml ampoules vs. the ratio between oil and air.

A set of unknown samples (Round Robin samples form a working group in CIGRE, presented in Appendix A, Table I were analyzed in the same way with the calorimeter and the area below the curves were compared to the area below the curves of the known samples.

The results are presented in Table 3 and illustrated in Figure 22. By this the oxidative stability of the liquids was determined and the oils were classified.

Table 3. Overview of the area below curves vs. ratio oil/air for the Round Robin samples.

Sample number	Dens (g/ml at 25°C)	Assessment of the oxidation stability	Ratio oil/air	Area below curve (h*µW/g)
U1	0.880	High	2.80	22
U2	0.874	Very Low	2.71	592
U3	0.878	Very Low	2.53	488
U4	0.878	High	2.64	38
U5	0.879	High	2.47	9
U6	0.873	High	2.84	10*
U7	0.878	High	3.40	2
U8	0.966	High	2.08	34
U9	0.911	Very Low	2.09	407
U10	0.890	Extreme Low	1.99	982
U11	0.916	Extreme Low	1.73	1317
U12	0.878	High	2.25	56
U13	0.866	Medium/low	1.69	297
U14	0.882	High/medium	1.98	174
U15	0.866	High	1.88	29
U16	0.879	High	2.01	41

* The area of the curve is given as negative, the net reactions are endothermic; most of the curve is below 0 µW/h

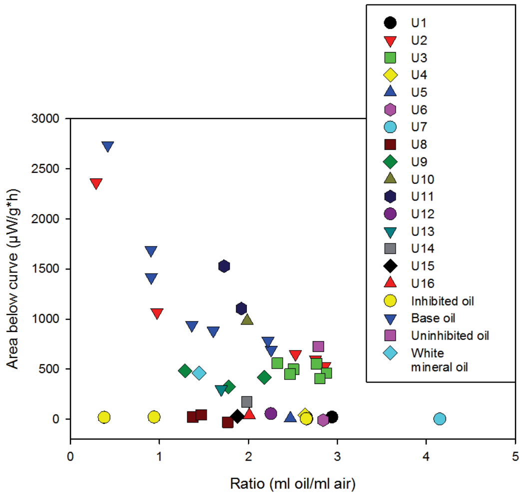

Figure 22. The area below curves (h*µW/g) vs. ratio oil/air for the unknown samples, inhibited, base oil, uninhibited and white mineral oil.

The results of the unknown samples were compared to analysis of the same samples done by other laboratories (Table 1 in section 5.1.1); showing that the methods based on the measurements of the onset of oxidation give similar results as those obtained by using the microcalorimeter.

An unknown sample (U3) was analyzed in the presence (denoted +) and absence (denoted -) of oxygen in the sample and one experiment where the oxygen in the sample was removed by inert gas purging, but the free volume of the ampoule was filled with air (denoted +/-). As seen in Figure 23 the area below the curves is very dependent on the availability of oxygen. The area under the curves decreases with increasing ratio of oil/air, showing that the oxygen present in the gas volume contributes to the oxidation reactions.

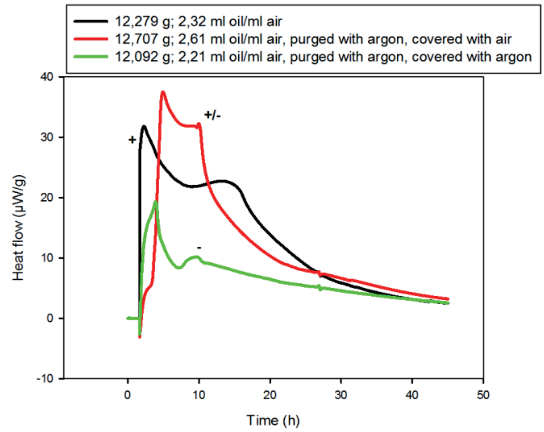

Figure 23. Microcalorimeter curves (heat flow vs. time) for sample U3. With air (+), without air covered with air (+/-), without air covered with inert gas (-).

For the inhibited oil (Figure 24) the signal is comparatively weak, and the trace profile changes with oxygen availability. With a large oxygen availability a small exothermic excursion is observed, the size decreases with increasing oil/air ratio, and with a high oil/air ratio the curve resembles that obtained after a nitrogen gas purge, where an apparently negative heat-flow is observed (i.e. an endothermic process). All the curves stabilize quickly to the baseline (0 µW/g heat flow). The areas below the curves are small, but smaller for the samples purged with nitrogen than those with oxygen, as shown in Figure 24. The inhibited oil contains antioxidants and metal passivators that prevent the oxygen in the oil from reacting with the oil compounds. Antioxidants will react with the radicals formed during the initiation step preventing the propagation; this explains why there is no apparent oxidation of this oil.

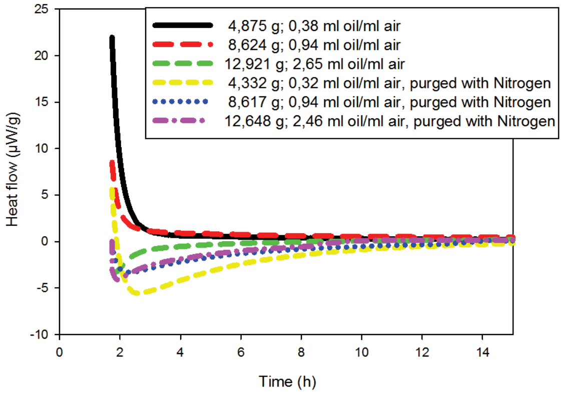

Figure 24. Microcalorimeter curves (heat flow vs. time) for inhibited oil.

Figure 25 shows experiments where base oil was made inhibited by mixing small amounts of inhibited oil in the base oil. The resulting traces are very similar to the trace of the inhibited oil shown in Figure 24.

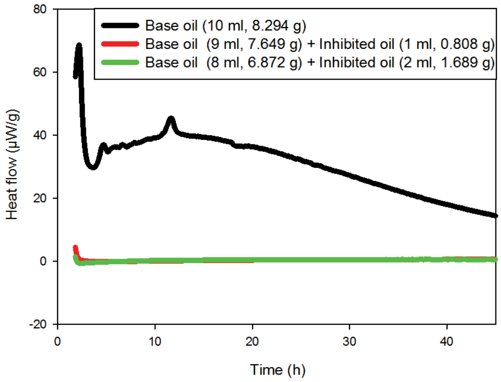

Figure 24. Microcalorimeter curves (heat flow vs. time) for base oil and base oil added inhibited oil.

6.1.2 Paper II: A Study of the Effects of Copper and Additives in Hydrocarbons and Ester with Isothermal Microcalorimetry

In this paper the isothermal microcalorimeter (described in section 5.1) has been used to study the effect of copper, dibenzene disulphide (DBDS) and a metal passivator I39 (Irgamet39^{TM} from Ciba) in dielectric liquids and in model oil. To limit the amount of uncertainties due to the composition of mineral oil, hexadecane was used as model oil in the main part of the experiments. In the calorimeter curves there was observed a clear peak caused by copper in hexadecane (Figure 26).

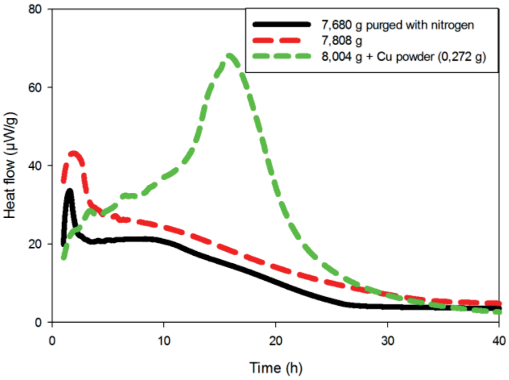

Figure 26. Microcalorimeter curves (heat flow vs. time) for hexadecane with copper powder (green dashed line) and without copper powder (red dashed line) and without copper powder purged with nitrogen (black line).

This peak was also observed in base oil (Figure 26) but not in inhibited oil (Figure 28) nor in the vegetable oil Envirotemp^{TM} FR3^{TM} (FR3, Cargill) (Figure 29). It is interpreted that this peak is caused by the catalytical effect of copper on the oxidation of hydrocarbons. Inhibited oil and FR3 contain so much antioxidants that the catalytical effect of formation of radicals due to copper is believed to be mitigated so much that the oxidation it is not observed in the calorimeter.

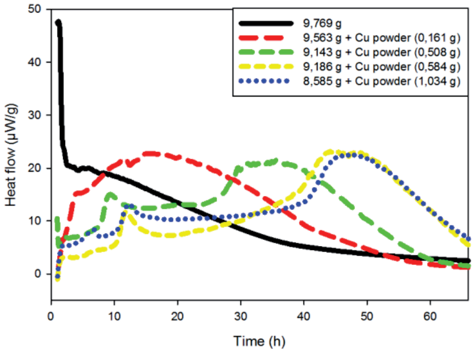

Figure 27. Microcalorimeter curve (heat flow vs. time) for base oil with different weights of added copper powder and base oil without copper (black line).

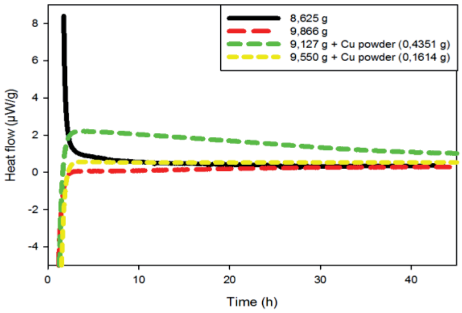

Figure 28. Microcalorimeter curves (heat flow vs. time) for the inhibited oil with copper powder (middle dashed line and short dashed line) and without copper (hole line and long dashed line).

It was observed that the catalytic oxidation peak appeared earlier with increasing amount of copper up to a certain level. Above this addition, the opposite was observed (Figure 29).

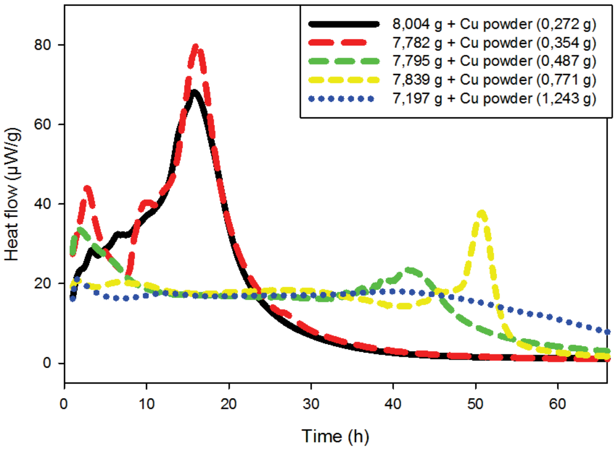

Figure 29. The microcalorimeter curves (heat flow vs. time) for hexadecane with Copper powder with varying weights (from 0.27 g to 1.24 g).

The peak height and time of the peak appearance was dependent on the copper surface area. The so-called critical phenomenon in catalysis is probably the reason for the difference in the peak appearance and height. This was also observed in base oil with copper (Figure 27).

The antioxidative effect of DBDS was evident when added to the liquids (Figure 30).

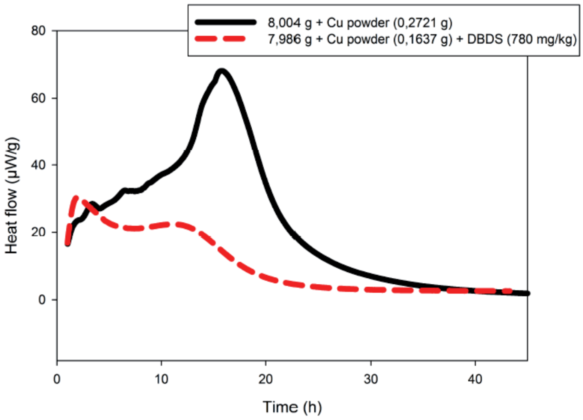

Figure 30. The microcalorimeter curve (heat flow vs. time) for hexadecane containing copper powder with (red broken line) and without (black line) DBDS.

The I39 seems to have no effect on the catalytical effect of copper in hexadecane as shown in Figure 32.

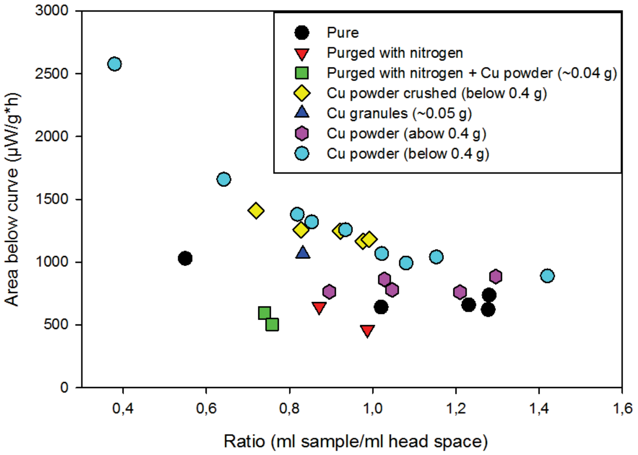

Figure 31. The area below curve (µW/g*h) for hexadecane under different conditions. Symbols: see insert in the figure. The errors were calculated to 15 %.

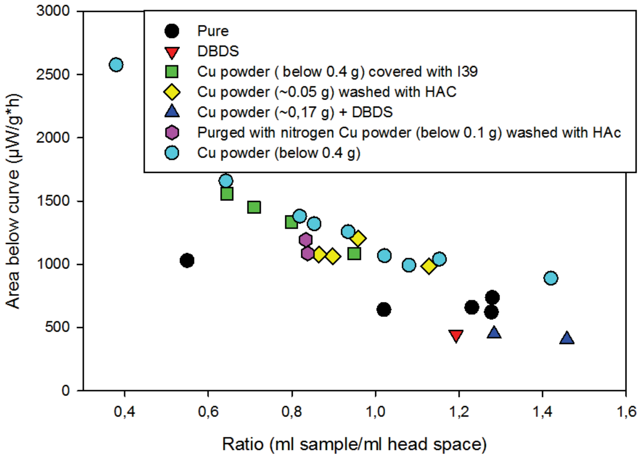

Figure 32. The area below curve (µW/g*h) for hexadecane under different conditions. Symbols: see insert in the figure. The errors were calculated to 15 %.

In Figure 33 and Figure 34 the effect of I39, Cu and DBDS in base oil is seen. The I39 does not increase the oxidation and there is no obvious effect of DBDS on the oxidation. The total oxidation of base oil is not changed by addition of copper powder in the oil, but as seen in Figure 27 there is a clear peak caused by copper. By purging the base oil with nitrogen the oxidation is decreased as observed in Figure 34 (yellow rhomboids). By adding copper powder to the base oil and purging with nitrogen the effect of the purging is not observed as seen in Figure 34 (green squares).

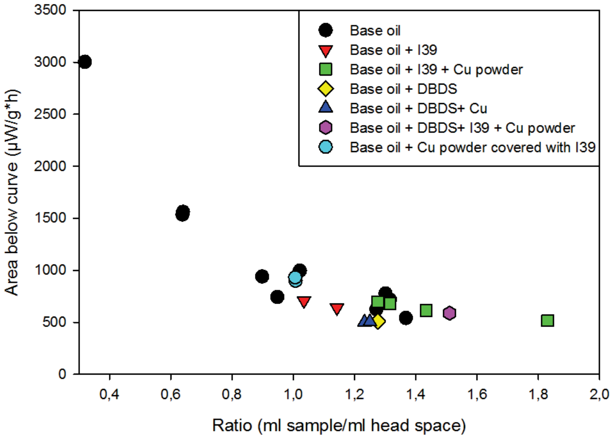

Figure 33. The area below curve vs. the ratio (up to 66 hours) between the sample volume and the volume of the head space for base oil with additives. Se insert for conditions. The error was found to be max 28 %.

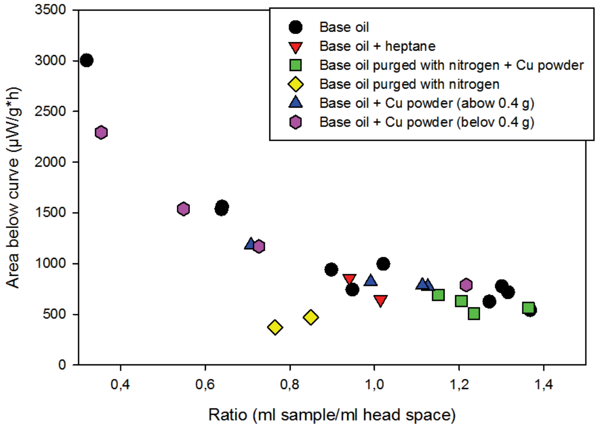

Figure 34. The area below curve vs. the ratio (up to 66 hours) between the sample volume and the volume of the head space for base oil at different conditions. Se insert for conditions. The error was found to be max 28 %.

6.2 Paper III: Ageing and Corrosion of Paper Insulated Copper Windings: The Effect of Irgamet39 in Aged Insulated Oil

In this paper the effect of adding I39 to the oil after corrosion and sulphide formation has started has been investigated. The effect of I39 has been studied together with measurements of the change in the concentration of free sulphide species in corrosive oil with copper present. Also the change in I39 concentration in the presence of cobber was investigated.

It is assumed that changes in the concentration of free sulphur species indicate that the sulphur is removed from the oil and either reacts with the copper or is absorbed in the paper. All the results show that the concentration of free sulphur species decreases with time when ageing the oil with copper at 150 °C as in Figure 35. In the samples with I39 the concentration decreases slower than without I39. Also here it seems that there is no difference with one or two layers of paper indicating that it is the copper that has an influence on the sulphide concentration, the sulphide species are probably not adsorbed or absorbed by the paper.

The fact that the concentration of sulphur species in the oil decreases slower with I39 in the oil indicates that the I39 hinders the sulphur from reacting with the copper. As seen in Figure 35 the concentration of sulphur species decreases fast if the I39 is not added before day 3. Moreover, the adsorption of I39 on the Cu-surface appears to be faster than the formation of copper sulphide. If the I39 is added after day three, the I39 seems to have little or no effect on the concentration of free sulphur species (Figure 35).

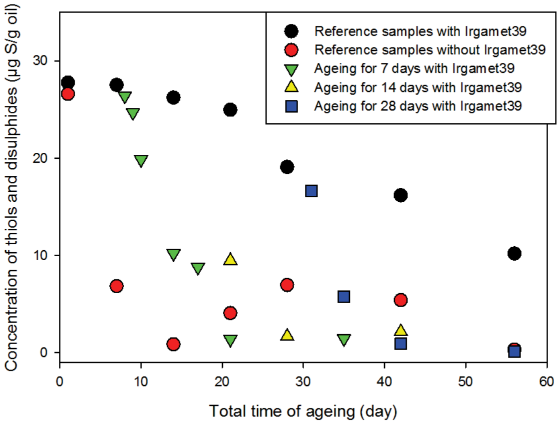

Figure 35. The concentration of sulphur species in transformer oil with copper wrapped with one layer of paper. The total time of ageing indicates the day of outtake of the samples. The deviation was found to be 5% at concentrations above 10 µg S/g oil.

The copper was also inspected visually and compared to reference samples. Furthermore, there are apparently small effects with regard to halting the corrosion caused by sulphide if the process has already started.

Measurements of the concentration of I39 in presence of cobber in white mineral oil during heating showed that the temperature had a large influence on the adsorption of I39 on the copper (Figure 36).

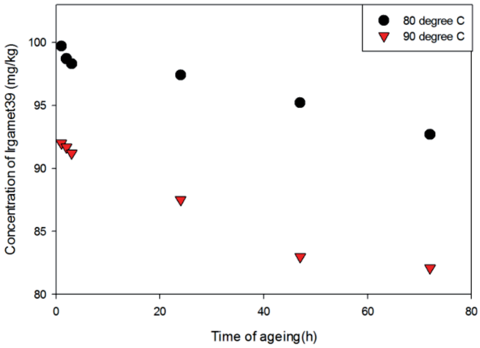

Figure 36. The change in concentration of I39 with time at 80 °C (black circles) and 90 °C (red triangles) measured with UV-Vis spectrophotometer.

To study the adsorption of I39 on the copper surface a quartz crystal microbalance (QCM) was used. The QCM records the change in mass of the copper due to I39 adsorption with time, and provides an estimate of the mass of adsorbed I39 at monolayer coverage. The solvent has an influence on the adsorbed amount of I39 (Table 4). The I39 was found to adsorb also on the surface of copper covered with sulphide species (Table 4) but as illustrated in Figure 35 the protecting effect of I39 is weakened even if adsorbed in the copper surface.

Table 4. Results of the QCM experiments; calculated mass at monolayer coverage, time at monolayer coverage, calculated molecular area of I39 at the surface and the adsorbed mass at saturation.

Sample, solvent and temperature (°C)	Time (h)	Monolayer mass (ng/cm^2)	Molecular surface area TTA (nm^2/molecule)	Molecular surface area I39 (nm^2/molecule)	ΔD/ΔF	Saturated adsorption mass (ng/cm^2)
H1 (40°C) Heptane	6.5	463±70	0.048	0.139	24.4	2322±710
H3 (RT) Heptane purged with argon	15.3	728±15	0.031	0.088	14.6	8615±1895
H4 (RT) Heptane purged with argon	13.2	1563±41	0.015	0.041	17.8	3656±407
H/T5 Heptane 50%/toluene 50 % (40°C)	4.2	245±16	0.091	0.262	6.0	
T6 Toluene(40°C)	9.0	211±73	0.105	0.304	6.7	
HA1 Heptane (25°C)	7.8	1086±12	0.020	0.059	22.2	4340±516
HA2 Heptane (25°C)	2.1	1106±46	0.020	0.058	17.8	2760±758

The passivation effect is good with regard to protecting copper against corrosive sulphur if the I39 is added before the copper is in contact with the corrosive oil. The I39 must be used in a concentration above 25 mg/kg oil. The I39 may have an effect if added very early in the transformers life, but after the corrosion has started the effect of I39 is not seen, this may be a combination of the degradation of I39 in the oil due to the oxidation products in aged oil and less effective protection of corroded copper surface.

7 Conclusion

Breakdowns in high voltage transformers are of major concern both because of high cost due to long outage time and cost from lost production and supply, and due to large potential consequences like fire and explosions. These risks can be reduced by use of good design and materials and by introduction of monitoring for failure recognition and repair and for optimum end-of-life estimation. Better knowledge on material testing and performance will help reducing risks. This is important both for specification and testing of new materials and for diagnostic during service life.

This work has shown that the isothermal microcalorimeter is a good method to study the oxidation stability of dielectric liquids from transformers in use and new dielectric liquids of different origin. The isothermal microcalorimeter is also suited to study the effect of additives on the oxidation stability of the dielectric liquid. The isothermal microcalorimeter has been used to classify a set of used and unused dielectric liquids into stable and non-stable oils with regard to oxidation stability. It has been shown that the isothermal microcalorimeter can be used to study the catalytical effect of copper on the oxidation of hydrocarbon liquids. Also the effect of an antioxidant added to hydrocarbons can be studied by means of this technique.

Formation of copper-sulphide species has been of large concern the last decades, due to breakdowns caused by dielectric breakthrough as outcome of corrosion of copper windings and copper-sulphide formation on insulating paper. To avoid this, metal deactivators and metal passivators have been added to the dielectric liquids. It is of interest to understand as good as possible how these passivators work in the transformer. Therefore the effect of the most used metal passivator, I39, has been studied. The results have indicated that there is reduced effect of adding I39 to the aged dielectric liquid where the corrosion of the copper surface has started. But if the I39 is added to the dielectric liquid before use the I39 has a very good effect with regard to passivation of the metal surface. The temperature and properties of the solvent are important parameters influencing the adsorption of I39.

8 Further work

Since isothermal microcalorimetry has been shown to be a good method for investigation of oxidation of organic liquids. It is therefore of great interest to use the calorimeter to study different esters and oils. It is of interest to find alternative environmental friendly liquids for use in transformers, it is of interest to continue the study of esters with regard to the environmental properties. Is it possible to investigate the difference in the saturation of oil (number of double bounds in the chains) in vegetable oils with regard to the heat flow in the calorimeter, and can the vegetable oils being compared with regard to the heat flow?

The work on the method for determination of oxidation stability with isothermal microcalorimetry could be used as an input to a protocol made for the microcalorimeter method on oxidation and stability of oil.

The experiments done in this work show that the critical phenomenon in catalysis can be observed by isothermal microcalorimetry. It would be of interest to compare this with other studies done on the critical phenomenon and repeat experiments that has been done by other researchers using other techniques.

The experiments with the QCM can be looked at as preliminary experiments and the results have shown that this is a method of great promise with regard to mapping the adsorption of I39 and other passivators. For example it would be interesting to study and compare BTA with I39 since there are a lot of results done with BTA by other researchers, available in the literature.

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Appendix

A. Overview of all microcalorimetry experiments

Table I. Overview of the liquids used in the microcalorimeter experiments

Liquid	Supplier	Density	Specifications
Uninhibited oil	Transformer oil supplier	0,88	Naphthenic oil
Inhibited oil	Transformer oil supplier	0,88	Naphthenic oil
White mineral oil	Sigma Aldrich	0,84	Light naphthenic oil
Base oil	Transformer oil supplier	0,87	Naphthenic oil
Hexadecane	Sigma Aldrich	0,77	
Heptane	Sigma Aldrich	0,68	
U1	Unknown (CIGRE' Round Robin sample)	0.880	Naphthenic based (uninhibited mineral oil)
U2	Unknown (CIGRE' Round Robin sample)	0.874	Naphthenic-paraffinic based (uninhibited mineral oil)
U3	Unknown (CIGRE' Round Robin sample)	0.878	Severely hydrotreated naphthenic base oil (uninhibited mineral oil)
U4	Unknown (CIGRE' Round Robin sample)	0.878	Naphthenic based, hydrotreated oil (uninhibited mineral oil)
U5	Unknown (CIGRE' Round Robin sample)	0.879	Severely hydrotreated naphthenic base oil (inhibited mineral oil)
U6	Unknown (CIGRE' Round Robin sample)	0.873	Naphthenic based, inhibited with -0,30% DBPC (inhibited mineral oil)
U7	Unknown (CIGRE' Round Robin sample)	0.878	Naphthenic based, hydrotreated phenolic inhibited (inhibited mineral oil)
U8	Unknown (CIGRE' Round Robin sample)	0.966	Synthetic ester
U9	Unknown (CIGRE' Round Robin sample)	0.911	High oleic vegetable oil, highly refined with inhibitor package (not DBPC)
U10	Unknown (CIGRE' Round Robin sample)	0.890	Blend of vegetable oil and esters of fatty acids and heavy monoalcohol, no additives
U11	Unknown (CIGRE' Round Robin sample)	0.916	Vegetable oil, highly refined and with an inhibitor package
U12	Unknown (CIGRE' Round Robin sample)	0.878	Hydrotreated used oil (refurbished or reclaimed mineral oil)
U13	Unknown (CIGRE' Round Robin sample)	0.866	Depolarized reclaimed oil (refurbished or reclaimed mineral oil)
U14	Unknown (CIGRE' Round Robin sample)	0.882	Depolarized reclaimed oil (refurbished or reclaimed mineral oil)
U15	Unknown (CIGRE' Round Robin sample)	0.866	Naphthenic-paraffinic base oil with total 0.4% inhibitors, consisting of hindered phenol type and diarylamin type (special inhibitors mineral oil)
U16	Unknown (CIGRE' Round Robin sample)	0.879	Naphthenic based oil, hydrotreated phenolic and aminic inhibited (special inhibitor mineral oil)

Table II. Overview of all experiments performed with Hexadecane in the isothermal microcalorimeter

Sample	**Temperature (°C)**	**head space (air or purged with nitrogen)**	**Weight tot (g)**	**Weight hexadecane (g)**	**Weight Cu (g)**	**Weight DBDS (g)**	**Total sample volume (ml)**	**Ratio ml oil/ml head space**	**Area below curve (µW/g*h) 45 h**
Hexadecane	110	air	8,67	8,67			11,22	1,28	622
Hexadecane	110	air	8,53	8,53			11,03	1,23	659
Hexadecane	110	air	7,81	7,81			10,10	1,02	642
Hexadecane + Cu powder(0,2721 g)	110	air	8,28	8,00	0,27		10,38	1,08	992
Hexadecane + Cu powder (0,4872 g)	110	air	8,28	7,79	0,49		10,14	1,03	863
Hexadecane + Cu powder (0,4589g)	110	air	8,88	8,42	0,46		10,95	1,21	761
Hexadecane	110	air	5,48	5,48			7,09	0,55	1029
Hexadecane + Cu powder (0,3544 g)	110	air	8,14	7,78	0,35		10,11	1,02	1068
Hexadecane + Cu powder (0,7707 g)	110	air	8,61	7,84	0,77		10,23	1,05	779
hexadecane + Cu powder (1,2428 g)	110	air	8,44	7,20	1,24		9,45	0,90	764
hexadecane + Cu powder (0,0390 g)	110	air	4,29	4,25	0,04		5,50	0,38	2577
Hexadecane + Cu powder (0,04115 g)	110	air	9,11	9,07	0,04		11,74	1,42	889
Hexadecane + DBDS (350 mg/kg)	110	air	8,71	8,41		0,30	10,88	1,19	445
Hexadecane	110	air	8,68	8,68			11,23	1,28	737

Sample	**Temperature (^{o}C)**	**head space (air or purged with nitrogen)**	**Weight tot (g)**	**Weight hexadecane (g)**	**Weight Cu (g)**	**Weight DBDS (g)**	**Total sample volume (ml)**	**Ratio ml oil/ml head space**	**Area below curve (µW/g*h) 45 h**
Hexadecane + Cu powder (0,5362 g)	110	air	9,22	8,68	0,54		11,30	1,30	885 (43 h)
Hexadecane + Cu powder (0,1637 g) + DBDS (780 mg/kg)	110	air	8,76	7,99	0,16	0,61	11,20	1,28	449 (43 h)
Hexadecane + Cu powder (0,0566 g)	110	air	8,33	8,27	0,06		10,70	1,15	1040 (43 h)
Hexadecane + Cu powder + DBDS (350 mg/kg)	110	air	9,65	9,16	0,18	0,31	11,90	1,46	407 (43 h)
Hexadecane + Cu granules	110	air	7,07	7,02	0,05		9,10	0,83	1066
Hexadecane + Cu powder	110	air	7,14	7,12	0,02		9,20	0,85	1320
Hexadecane + Cu crushed powder	110	air	7,16	6,99	0,17		9,10	0,83	1257 (41 h)
Hexadecane + Cu crushed powder	110	air	6,59	6,46	0,14		8,40	0,72	1410 (41 h)
Hexadecane + Cu crushed powder	110	air	7,67	7,64	0,03		9,90	0,98	1166
Hexadecane + Cu crushed powder	110	air	8,02	7,67	0,35		10,00	0,99	1181

Sample	**Temperature (^oC)**	**head space (air or purged with nitrogen)**	**Weight tot (g)**	**Weight hexadecane (g)**	**Weight Cu (g)**	**Weight DBDS (g)**	**Total sample volume (ml)**	**Ratio ml oil/ml head space**	**Area below curve (µW/g*h) 45 h**
Hexadecane + Cu crushed powder	110	air	7,43	7,41	0,02		9,60	0,92	1246
Hexadecane + cu powder	110	air	7,51	7,46	0,05		9,66	0,93	1257
Hexadecane + Cu crushed powder covered with I39	110	air	7,67	7,51	0,22		9,74	0,95	1085
Hexadecane + Cu powder covered with I39	110	air	6,58	6,40	0,16		8,30	0,71	1451
Hexadecane + Cu powder covered with I39	110	air	13,47	13,24	0,23		17,16	6,03	398
Hexadecane + Cu powder covered with I39	110	air	12,75	12,48	0,28		16,17	4,22	428
Hexadecane purged with nitrogen	110	Nitrogen	7,20	7,20			9,31	0,87	647 (43 h)
Hexadecane purged with nitrogen	110	Nitrogen	7,68	7,68			9,94	0,99	463 (43 h)
Hexadecane+ Cu powder covered with I39	110	air	6,14	6,05	0,09		7,84	0,64	1558

Sample	**Temperature (^{o}C)**	**head space (air or purged with nitrogen)**	**Weight tot (g)**	**Weight hexadecane (g)**	**Weight Cu (g)**	**Weight DBDS (g)**	**Total sample volume (ml)**	**Ratio ml oil/ml head space**	**Area below curve (µW/g*h) 45 h**
Hexadecane+ Cu powder covered with I39	110	air	6,94	6,86	0,09		8,88	0,80	1334
Hexadecane + Cu powder	110	air	6,98	6,96	0,02		9,00	0,82	1380
hexadecane + Cu powder	110	air	6,09	6,04	0,05		7,82	0,64	1659
Hexadecane purged with nitrogen + Cu powder	110	Nitrogen	6,61	6,57	0,04		8,51	0,74	595 (43 h)
Hexadecane purged with nitrogen + Cu powder	110	Nitrogen	6,70	6,66	0,03		8,62	0,76	504 (43 h)
Hexadecane + Cu powder acid washed	110	air	7,36	7,31	0,05		9,46	0,90	1063 (17 h)
Hexadecane + cu powder acid washed	110	air	7,21	7,17	0,04		9,27	0,86	1077 (17 h)
Hexadecane purged with nitrogen+ Cu powder acid washed	110	Nitrogen	7,12	7,04	0,08		9,12	0,84	1086
Hexadecane purged with nitrogen + Cu powder acid washed	110	Nitrogen	7,05	7,03	0,02		9,09	0,83	1193

Sample	Temperature (°C)	head space (air or purged with nitrogen)	Weight tot (g)	Weight hexadecane (g)	Weight Cu (g)	Weight DBDS (g)	Total sample volume (ml)	Ratio ml oil/ml head space	Area below curve (µW/g*h) 45 h
hexadecane + acid washed Cu powder	110	air	7,61	7,56	0,05		9,79	0,96	1204 (45 h)

Table III Overview of all experiments performed with mineral oils, unknown samples and vegetable oil in the isothermal microcalorimeter

Sample	Temperature °C	Head space (air or purged with nitrogen	Steel(s) /glass (gl)	Weight total (g)	Weight oil(g)	Weight Cu (g)	Weight Irgamet39 or heptan (g)	Weight DBDS (g)	Volume (ml)	Ratio ml oil/ml head space	Area
Base oil	110	Air	g	10,08	10,08				11,6	1,4	541
Base oil	110	Air	g	8,49	8,49				9,7	0,9	743
Base oil	110	Air	g	9,77	9,77				11,2	1,3	625
Base oil + I39 129 mg/kg oil)	110	Air	g	9,31	9,18		0,13		10,7	1,1	641
Base oil + I39(I39 (132 mg/kg oil)	110	Air	g	8,87	8,75		0,13		10,2	1,0	709
Base oil + Heptane	110	Air	g	8,79	8,69		0,10		10,1	1,0	645
Base oil + heptane	110	Air	g	8,46	8,33		0,13		9,7	0,9	857
Base oil + Cu powder	110	Air	g	9,77	9,19	0,58			10,6	1,1	775
Base oil + Cu powder	110	Air	g	9,62	8,59	1,03			10,0	1,0	820
Base oil + Cu powder	110	Air	g	9,65	9,14	0,51			10,5	1,1	785
Base oil + Cu powder Without O2	110	nitrogen	g	10,30	10,04	0,25			11,5	1,4	564
Base oil + Cu powder Without O2	110	nitrogen	g	9,62	9,53	0,09			10,9	1,2	630

Sample	**Temperature ^oC**	**Head space (air or purged with nitrogen**	**Steel(s) /glass (gl)**	**Weight total (g)**	**Weight oil(g)**	**Weight Cu (g)**	**Weight Irgamet39 or heptan (g)**	**Weight DBDS (g)**	**Volume (ml)**	**Ratio ml oil/ml head space**	**Area**
Base oil + Cu powder Without O2	110	nitrogen	g	9,56	9,31	0,24			10,7	1,2	690
Base oil + Cu powder Without O2	110	nitrogen	g	10,11	9,59	0,52			11,1	1,2	507
Base Oil	110	Air	s	12,10	12,10				13,9	1,3	717
Base Oil	110	Air	s	12,04	12,04				13,8	1,3	776
Base Oil	110	Air	s	10,07	10,07				11,5	0,9	940
Base Oil	110	Air	s	8,29	8,29				9,5	0,6	1536
Base Oil	110	Air	s	5,16	5,16				5,9	0,3	3004
Base Oil	110	Air	s	8,31	8,31				9,5	0,6	1561
Base Oil	110	Air	s	10,76	10,76				12,3	1,0	996
Base Oil	110	Air	s	15,17	15,17				17,4	2,5	530
Base oil	80	Air	s	12,93	12,93				14,8	1,5	
Base oil	80	Air	s	13,22	13,22				15,2	1,6	
Base oil without O2	110	nitrogen	g	9,20	9,20				10,6	0,8	371
Base oil without O2	110	nitrogen	g	9,75	9,75				11,2	0,8	469
Base oil +Cu powder + I39 (109,5 mg/kg)	110	Air	g	10,04	9,75	0,17	0,11		11,4	1,3	682
Base oil + Cu powder	110	Air	g	9,72	9,56	0,16			11,0	1,2	788
Base oil + Cu powder) + I39 (99,47 mg/kg)	110	Air	g	10,44	10,12	0,21	0,11		11,8	1,4	614
Base oil + Cu powder + I39 (221,7 mg/kg)	110	Air	g	10,04	9,46	0,36	0,22		11,2	1,3	699
Base oil + Cu powder + I39 (195,9 mg/kg)	110	Air	g	11,36	10,69	0,44	0,22		12,9	1,8	516

Sample	**Temperature ^{o}C**	**Head space (air or purged with nitrogen**	**Steel(s) /glass (gl)**	**Weight total (g)**	**Weight oil(g)**	**Weight Cu (g)**	**Weight Irgamet39 or heptan (g)**	**Weight DBDS (g)**	**Volume (ml)**	**Ratio ml oil/ml head space**	**Area**
Base oil +DBDS (123 mg/kg)	110	Air	g	9,78	9,67			0,12	11,2	1,3	511
Base oil + DBDS (116,6 mg/kg) + Cu powder	110	Air	g	9,97	9,46	0,41		0,11	11,0	1,2	502
Base oil + Cu powder + DBDS (90,7 mg/kg) + i39 (101,3 mg/kg)	110	Air	g	10,79	10,25	0,33	0,11	0,09	12,0	1,5	588
Base oil + Cu powder + DBDS (98,3 mg/kg)	110	Air	g	9,93	9,57	0,27		0,09	11,1	1,3	504
Base oil + Cu powder	110	Air	g	7,66	7,19	0,47			8,3	0,7	1184
Base oil + Cu powder	110	Air	g	7,63	7,31	0,31			8,4	0,7	1169
Base oil + Cu powder	110	Air	g	4,67	4,55	0,12			5,2	0,4	2293
Base oil + Cu powder	110	Air	g	6,29	6,17	0,11			7,1	0,5	1539
base oil + acid washed Cu powder	110	Air	g	8,23	8,19	0,04			10,6	1,1	988 (45 h)

Sample	Temperature °C	Head space air or purged with nitrogen	Steel (s)/glass (g)	Weight total (g)	Weight oil(g)	Weight Cu (g)	Weight Irgamet39or heptan (g)	Volume (ml)	Ratio ml oil/ml head space	Area (45 h)
New inhibited	110	Air	s	11,45	11,45			13,0	1,1	-3
Aged inhibited	110	Air	s	10,34	10,34			11,7	0,9	5
new inhibited + I39 (1645 mg/kg)	110	Air	s	12,70	12,68		0,021	14,4	1,4	18
aged inhibited + I39 (1877 mg/kg)	110	Air	s	12,84	12,81		0,024	14,6	1,5	32
New inhibited	110	Air	s+i39	12,93	12,93			14,7	1,5	17
New Inhibited + I39 (1958 mg/kg)	110	Air	s+i39	12,18	12,15		0,024	13,8	1,3	21
New inhibited	110	Air	g	9,87	9,87			11,2	1,3	6
New inhibited + I39 (121 mg/kg)	110	Air	g	9,77	9,64		0,124	11,1	1,2	11
White mineral oil	120	Air	s	11,50	11,50			13,1	1,2	958
White mineral oil	120	Air	s	14,26	14,26			16,2	2,0	584
White mineral oil	120	Air	s	6,90	6,90			7,9	0,5	1818
White mineral oil	120	Air	s	4,59	4,59			5,2	0,3	3576
White mineral oil	120	Air	s	9,03	9,03			10,3	0,7	1420
White mineral oil	120	Air	s	13,13	13,13			15,0	1,6	720
Inhibited Oil	110	Air	s	4,87	4,87			5,5	0,3	18
Inhibited Oil	110	Air	s	8,62	8,62			9,8	0,7	21
Inhibited Oil	110	Air	s	12,92	12,92			14,7	1,5	5
Inhibited Oil	110	Nitrogen	s	4,33	4,33			4,9	0,3	-18
Inhibited Oil	110	Nitrogen	s	8,61	8,61			9,8	0,7	-10

Sample	Temperature ^oC	Head space air or purged with nitrogen	Steel (s)/glass (g)	Weight total (g)	Weight oil(g)	Weight Cu (g)	Weight Irgamet39or heptan (g)	Volume (ml)	Ratio ml oil/ml head space	Area (45 h)
Inhibited Oil	110	Nitrogen	s	12,65	12,65			14,4	1,4	-6
U3	110	Air	s	12,55	12,55			14,3	1,4	499
U2	110	Air	s	12,53	12,53			14,3	1,4	648
U1	110	Air	s	12,78	12,78			14,5	1,5	23
U3	110	Nitrogen	s	12,21	12,21			13,9	1,3	248
U2	110	Nitrogen	s	12,38	12,38			14,2	1,4	438
U1	110	Nitrogen	s	13,32	13,32			15,1	1,6	-4
U6	110	Air	s	12,73	12,73			14,6	1,5	-10
U5	110	Air	s	12,52	12,52			14,2	1,4	9
U4	110	Air	s	12,91	12,91			14,7	1,5	38
U3	110	Air	s	12,90	12,90			14,7	1,5	554
U2	110	Air	s	12,83	12,83			14,7	1,5	598
U1	110	Air	s	13,13	13,13			14,9	1,6	21
U2	110	Air	s	12,95	12,95			14,8	1,5	530
U2	110	Air	s	8,62	8,62			9,9	0,7	1068
U2	110	Air	s	3,91	3,91			4,5	0,2	2364
U3	110	Air	s	12,28	12,28			14,0	1,3	560
U3	110	Purged with nitrogen, covered with air	s	12,71	12,71			14,5	1,5	525
U3	110	Nitrogen	s	12,09	12,09			13,8	1,3	280
U3	110	Air	s	12,50	12,50			14,2	1,4	449
U3	110	Air	s	13,03	13,03			14,8	1,6	460
U3	110	Air	s	12,94	12,94			14,7	1,5	405
U3	110	Air	s	12,49	12,49			14,2	1,4	246 (25 h)
U3	110	Air	s	13,20	13,20			15,0	1,6	267(25 h)
U3	110	Air	s	12,91	12,91			14,7	1,5	322 (25 h)
10 ml Base Oil +5 ml Inhibited Oil	110	Air	s	11,96	11,96			13,7	1,3	4
5 ml Base Oil 10 ml Inhibited Oil	110	Air	s	12,07	12,07			13,8	1,3	2

Sample	**Temperature °C**	**Head space air or purged with nitrogen**	**Steel (s)/glass (g)**	**Weight total (g)**	**Weight oil(g)**	**Weight Cu (g)**	**Weight Irgamet39or heptan (g)**	**Volume (ml)**	**Ratio ml oil/ml head space**	**Area (45 h)**
Base Oil 14 ml Inhibited Oil 1 ml	110	Air	s	12,29	12,29			14,1	1,4	-175
Base Oil 13 ml Inhibited Oil 2 ml	110	Air	s	12,13	12,13			13,9	1,3	-9
Base Oil 14,5 ml Inhibited Oil 0,5 ml	110	Air	s	12,49	12,49			14,3	1,4	2
Base Oil 14 ml Inhibited Oil 1 ml	110	Air	s	12,91	12,91			14,8	1,5	0
Base Oil 9 ml Inhibited Oil 1 ml	110	Air	s	8,46	8,46			9,7	0,7	47
Base Oil 8 ml Inhibited Oil 2 ml	110	Air	s	8,56	8,56			9,8	0,7	42
U7	110	Air	s	12,76	12,76			14,5	1,5	3
U8	110	Air	s	12,34	12,34			12,8	1,1	-31
U9	110	Air	s	12,49	12,49			13,7	1,3	416
U10	110	Air	s	11,84	11,84			13,3	1,2	982
U11	110	Air	s	11,60	11,60			12,7	1,1	1528
U12	110	Air	s	12,16	12,16			13,9	1,3	56
U13	110	Air	s	10,89	10,89			12,6	1,1	297
U14	110	Air	s	11,72	11,72			13,3	1,2	174
U15	110	Air	s	11,30	11,30			13,0	1,1	29
U16	110	Air	s	11,74	11,74			13,4	1,2	41
U8	110	Air	s	11,18	11,18			11,6	0,9	21
Empty	110	Air	s	0,00	0,00			0,0	0,0	687
Base Oil/Uninhibited Oil	110	Air	s	12,59	12,59			14,4	1,4	742

Sample	Temperature °C	Head space air or purged with nitrogen	Steel (s)/glass (g)	Weight total (g)	Weight oil(g)	Weight Cu (g)	Weight Irgamet39or heptan (g)	Volume (ml)	Ratio ml oil/ml head space	Area (45 h)
Uninhibited Oil	110	Air	s	12,95	12,95			14,9	1,6	725
Uninhibited Oil	110	Air	s	12,11	12,11			13,9	1,3	432(24h)
Uninhibited Oil	110	Air	s	12,71	12,71			14,6	1,5	416(24h)
Uninhibited Oil	110	Air	s	12,96	12,96			14,9	1,6	388(24h)
White mineral oil	110	Air	s	11,93	11,93			13,6	1,3	10
White mineral oil	110	Air	s	8,04	8,04			9,2	0,6	15
White mineral oil	110	Air	s	4,92	4,92			5,6	0,3	21
U2+HAc strømbrudd	110	Air	s	10,12	10,12			11,6	0,9	
U2+HAc strømbrudd	110	Air	s	10,38	10,38			11,9	0,9	
U2 strømbrudd	110	Air	s	9,89	9,89			11,3	0,9	
U9	110	Air	s	10,26	10,26			11,3	0,9	482
U11	110	Air	s	12,05	12,05			13,1	1,2	1035
White mineral oil	110	Air	s	10,39	10,39			11,8	0,9	459
White mineral oil	110	Air	s	2,66	2,66			3,0	0,1	1043
White mineral oil	110	Air	s	7,31	7,31			8,3	0,5	528
White mineral oil	110	Air	s	11,12	11,12			12,7	1,1	293
U2	90	Air	s	12,97	12,97			14,8	1,6	9
U14	90	Air	s	12,11	12,11			13,7	1,3	-2
U6	90	Air	s	13,13	13,13			13,6	1,3	-1
U8	110	Air	s	11,50	11,50			11,9	1,0	2
U9	110	Air	s	11,65	11,65			12,8	1,1	43
U11 Unstable ch	110	Air	s	14,15	14,15			15,4	1,7	323
FR3	110	Air	s	7,34	7,34			8,0	0,5	2039
FR3	110	Air	s	7,85	7,85			8,5	0,5	1827

Sample	**Temperature °C**	**Head space air or purged with nitrogen**	**Steel (s)/glass (g)**	**Weight total (g)**	**Weight oil(g)**	**Weight Cu (g)**	**Weight Irgamet39or heptan (g)**	**Volume (ml)**	**Ratio ml oil/ml head space**	**Area (45 h)**
FR3 unstable ch	110	Air	s	11,14	11,14			12,1	1,0	1289
Uninhibited oil+ adipic acid (0,1195 g)	110	Air	s	9,47	9,35			10,9	0,8	1162 (110 h) /742
Unhibited oil + adipic acid (0,0206 g)	110	Air	s	11,58	11,56			13,3	1,2	983 (110 h)/ 573
Uninhibited oil + adipic acid (0,0185 g)	110	Air	s	14,03	14,01			16,1	1,9	657 (110 h) / 484
Uninhibited oil + naphthenic acid (0,02037 g)	110	Air	s	12,70	12,68			14,6	1,5	499(70h) /391
Uninhibited oil + naphthenic acid (0,01973g)	110	Air	s	13,20	13,19			15,2	1,6	516 (70h)/416
Uninhibited oil + naphthenic acid (0,0231 g)	110	Air	s	12,32	12,30			14,1	1,4	450 (73h)/ 364
Uninhibited oil + naphthenic acid (0,02085g)	110	Air	s	11,17	11,15			12,8	1,1	546 (73h) /437

Sample	**Temperature ^{o}C**	**Head space air or purged with nitrogen**	**Steel (s)/glass (g)**	**Weight total (g)**	**Weight oil(g)**	**Weight Cu (g)**	**Weight Irgamet39or heptan (g)**	**Volume (ml)**	**Ratio ml oil/ml head space**	**Area (45 h)**
Uninhibited oil + naphthenic acid (0,0178 g)	110	Air	s	15,56	15,56			17,9	2,7	309,2
Uninhibited oil + naphthenic acid (0,08454 g)	110	Air	s	11,80	11,80			13,6	1,3	392,9
Uninhibited oil	110	Air	s	8,48	8,48			9,7	0,7	888,0
Uninhibited oil	110	Air	s	13,27	13,27			15,3	1,7	442,0
Uninhibited oil + naphthenic acid (0,02200 g)	80	Air	s	11,69	11,67			13,4	1,2	28 (116 h)
Uninhibited oil + naphthenic acid (0,04314 g)	80	Air	s	13,64	13,60			15,6	1,8	30 (116 h)
Uninhibited oil	80	Air	s	12,52	12,52			14,4	1,4	9 (68 h)
Uninhibited oil + naphthenic acid (0,0257 g)	80	Air	s	12,43	12,41			14,3	1,4	14 (68 h)
Inhibited Oil	110	Air	g	10,32	10,32			11,7	0,9	30 (95 h)/16
Inhibited Oil	110	Air	g	10,36	10,36			11,8	0,9	25 (95 h)/10,365
heptane	90	Air	g	8,30	8,30			12,2	1,0	86 (72h)
heptane with Cu	90	Air	g	7,60	7,08	0,517		10,5	1,1	-133 (72h)
heptane with Cu	90	Air	g	8,27	7,97	0,299		11,8	1,4	9 (72h)

Sample	Temperature °C	Head space air or purged with nitrogen	Steel (s)/glass (g)	Weight total (g)	Weight oil(g)	Weight Cu (g)	Weight Irgamet39or heptan (g)	Volume (ml)	Ratio ml oil/ml head space	Area (45 h)
heptane With Cu and I39	90	Air	g	7,95	7,55	0,315	0,092	11,3	1,3	25 (72 h)
FR3	110	Air	g	7,98	7,98			8,7	0,6	1421
Inhibited oil + Cu (0,4351 g)	110	Air	g	9,56	9,13	0,435		10,4	1,1	65
Inhibited oil + Cu (0,1614 g)	110	Air	g	9,71	9,55	0,161		10,9	1,2	15
FR3 + Cu (0,3325 g)	110	Air	g	8,57	8,24	0,333		9,0	0,8	1369
FR3 + Cu (0,3627 g)	110	Air	g	10,82	10,46	0,363		11,4	1,3	1028
FR3 + Cu powder (0,2156 g)	11	Air	g	8,21	7,99	0,216		8,7	0,8	1296
FR3 + Cu powder (0,3074 g)	11	Air	g	9,32	9,01	0,307		9,8	1,0	1014
Uninhibited oil + Cu powder (0,0401 g)	110	Air	g	8,54	8,50	0,040		9,8	1,0	671
Uninhibited oil + Cu powder (0,0390 g)	110	Air	g	8,53	8,49	0,039		9,8	1,0	677

Paper I

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Paper II

A Study of the Effect of Copper and Additives in Hydrocarbon and Ester Based Insulating Liquids with Isothermal Microcalorimetry

Ingvild Tronstad and **Edd Anders Blekkan**
Norwegian University of Science and Technology (NTNU)
Department of Chemical Engineering
7491 Trondheim

and **Marit-Helen G. Ese**
SINTEF Energy Research
Department of Electric Power Technology
Sem Sælands vei 11
Trondheim

ABSTRACT

An isothermal microcalorimeter has been used to study the effect of solid copper in hexadecane, vegetable oil (ester) and mineral oil. The experiments have shown a catalytic effect of copper in oxidation of hydrocarbons and also the anti-oxidative effect of dibenzyl disulphide when combined with copper addition. The catalytic effect of copper is found in hydrocarbon as base oil and hexadecane, but not in experiments using inhibited oil and ester as the dielectric liquid.

Index Terms — **Aging, Copper, calorimetry, catalysis, dielectric liquids, oxidation stability.**

1 INTRODUCTION

IN many high voltage (HV) electrical equipment, liquid dielectrics are used as insulating materials and coolants. The stability of these liquids is of great concern and interest. Change in the dielectric and heat transport properties can have huge consequences, such as e.g. breakdown and fire in high voltage transformers. One of the issues that weaken the dielectric strength of the liquids is oxidation.

Much used dielectric liquid in HV transformers are naphthenic mineral oils, but also vegetable oils (natural esters) and synthetic esters are used in transformers.

Oxidation of organic liquids as mineral oils or esters is therefore a key issue. Oxidation involves transfer of electrons from one chemical component to another, the electron donor is oxidized and the electron acceptor is reduced. Oxidation often involves transfer of the element oxygen. In e.g. a mineral oil the oxidation occurs in three steps (chain oxidation); initiation where a radical is formed (the •denotes a radical, R a hydrocarbon); R→ R• by thermal generation, if oxygen is present the radical reacts with oxygen and gives the following possible reactions (propagation);

$$R\bullet + O_2 \rightarrow ROO\bullet \qquad (1)$$

$$ROO\bullet + RH \rightarrow ROOH + R\bullet \qquad (2)$$

$2ROO\bullet \rightarrow$ molecular products as aldehydes, alcohols, carboxylic acids and carbon dioxide and $R\bullet$ (3)

$$ROOH \rightarrow RO\bullet + \bullet OH \qquad (4)$$

$$RO\bullet + RH \rightarrow ROH + R\bullet \qquad (5)$$

$$\bullet OH + RH \rightarrow H_2O + R\bullet \qquad (6)$$

When two radicals combine, the chain reaction is terminated [2-4].

$$2R\bullet \rightarrow RR \qquad (7)$$

$$R\bullet + RO_2\bullet \rightarrow ROOR \qquad (8)$$

Copper is used as the conductor in transformers and the dielectric liquids is exposed to large areas of copper surface. Metallic copper is an active catalyst for many reactions, and copper is known to have a huge effect on the stability of the transformer oil. It has been observed that the production of hydroperoxide and carbonyl species increased with copper present in the oil [5]. The copper can act as a catalyst on the oxidation of hydrocarbons. Copper ions in the oil originate from corrosion of the copper by peroxides and radicals as in equation 9 [3, 6, 7].

$$2RO\bullet + Cu \rightarrow Cu^{2+} + 2RO^{-} \qquad (9)$$

Copper oxide also contributes to the oxidation of the hydrocarbons [5].

Catalyzed oxidation can occur as illustrated in equation 10-12 [8];

$$Cat + O_2 \leftrightarrow Cat....O_2 \xrightarrow{+RH} R\cdot \qquad (10)$$

$$Cat + RH \leftrightarrow Cat....RH \xrightarrow{+O_2} R\cdot \qquad (11)$$

$$Cat + RO_2\cdot \rightarrow Cat\ldots RO_2\cdot \rightarrow \begin{cases} \xrightarrow{+RH} P_s + R\bullet & (12a) \\ \text{Chain termination} & (12b) \end{cases}$$

where Cat is the heterogeneous catalyst and P is the product.

When the amount of a metallic catalyst reaches a certain amount, the role of the metal is believed to change from being a catalyst to being an inhibitor. This is extensively discussed and called the critical phenomenon [8-14]. Industrially, in order to limit or prevent oxidation of the oil, anti-oxidants (inhibitors) can be added.

Corrosion of metals in HV electrical equipment is also a problem; metal is oxidized (corroded) by electron transfer from the metal to an accepting chemical compound. This is often caused by oxygen or sulphur in transformers. To reduce the corrosion of copper, passivators and deactivators are added to the oil. Passivators protect the metal surface against oxidation while deactivators chelates with metal ions in the bulk solution and hinders the catalytic effect of the metal ions in the solution [6]. A much used metal passivator is Irgamet39, a tolutriazole (TTA) based molecule that is made more oil soluble through adding an N-aminomethyl group as an oleophilic "tail" as seen in Figure 1.

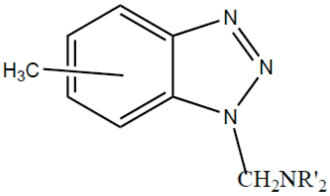

Figure 1 The structure of Irgamet39. From [1]

Oils that are added anti-oxidants, deactivators and passivators are termed inhibited oils. Oils without these additions, but that contains components that occur naturally in the oil and act as anti-oxidants, passivators and deactivators are termed uninhibited oils.

The oxidation of transformer liquids has been studied with a lot of different methods. A common method is accelerated ageing in bottles, where the oil kept at temperatures higher than typical in transformers, measuring the change in acid number and water content in the oil [15-17]. Alternatives include the "Pressure Vessel Oxidation Test" (RPVOT, ASTM D2112) and pressure differential scanning calorimetry (PDSC, where the onset time of oxidation (min) is reported [4]. Lately isothermal microcalorimetry has also been used as a faster method for studying the ageing of insulating materials [16-18].

In calorimeters the heat formed or consumed as a result of reactions and physical processes in a system is measured. Oxidation reactions, ligand bindings, desorption and adsorption on surfaces are some of the possible processes that can be measured [19]. When the heat evolution or consumption caused by oxidation is measured, the net heat-flow in the system is measured [19]. The net heat effect can be written as in eq. 13[20];

$$\frac{dQ}{dt} = \Phi + C\frac{dT}{dt} \qquad (13)$$

dQ/dt is the rate of heat produced by the sample, Φ is the heat exchange from the system to the surroundings, C is the heat capacity of the sample and dT is the change in temperature during the time dt [20]. Isothermal microcalorimeters measure the heat flow from a system with very high sensitivity (µW range), with a high degree of isothermality. In this communication we present results from oxidation studies performed in an isothermal microcalorimeter, investigating the effect of copper and oxidation inhibitors and passivators on a model hydrocarbon and different insulating oils.

2 EXPERIMENTAL

To investigate the effect of copper and additives in transformer oil a microcalorimeter has been used. Copper was added in form of granules, powder and crushed powder (Table 1). The additives studied were Irgamet39 (I39) and dibenzene disulphide (DBDS) described in Table 1. Base oil was used as mineral oil, since base oil is a complex mixture of components; hexadecane was used as simplified model oil. Also uninhibited oil and inhibited oil as well as a vegetable transformer oil (ester) were used (Table 2).

The instrument used was TAM III from TA Instruments, with four different calorimeters. The calorimeter used in these experiments is the 20 ml calorimeter with a temperature range of 15 to 150 ^{o}C with an accuracy of <± 0.1^{o}C. The precision of the micro calorimeter with 20 ml ampoules is ± 100 nW [21, 22]. Glass cups were placed inside the steel ampoules to avoid possible influence arising from the contact between steel and samples. The ampoules and glass cups were cleaned with water and 2-propanol and dried in air. The experiments were performed isothermally with the temperature in the calorimeter fixed at 110^{o}C.

A calorimeter procedure was followed;

- The temperature was set to 110^{o}C.
- A calibration of the heat flow was performed with empty channels.
- The ampoules with the samples were lowered to a preheat position where the ampules were preheated for 15 min.
- Ampoules lowered to the measuring position.
- The system is then stabilized for 45 minutes.
- The experiments were terminated when the signals were stable (1-3 days).
- After removing the ampoules from the calorimeter a final baseline was collected by the calorimeter.

Time zero was defined as the time when the ampoules were lowered to the preheat position, but the signal from the first hour is not reported. The base line was subtracted from the measurements in the calorimeter; this was done by the TAM Assistant software. The calorimeter contains a blank sample used to collect a base line during the experiments. The integrated area below the calorimetry curves (µW/g vs. time) was determined for the time between 1-45 hours for the hexadecane and ester and for 1-66 hours for the base oil experiments, using the macro “area below curves” in SigmaPlot. The error range of the area below the curves was found to be maximum 28 % for mineral oil and vegetable oil, and 5-15% for hexadecane by taking the standard deviations of the area of similar experiments.

Copper powder was crushed with a mill with grinding balls of stainless steel (Retsch mixer mill 400) for 5 min with a frequency of 30 s^{-1}.

In some experiments copper was covered with Irgamet39 by adding copper (~1 g) to a solution of Irgamet39 (~2000 mg/kg) in hexadecane and heating at 70^{o}C for at least 24 h. The copper was then washed with heptane and hexadecane and dried at 70^{o}C.

To remove the oxygen from hexadecane and base oil, the liquid was purged with nitrogen for at least one hour in an Erlenmeyer flask covered with a film (Parafilm), thereafter the hexadecane was transferred to the ampoule, weighed, and added copper, and then purged with nitrogen for 5 min in the ampule. The head space was blanketed with nitrogen.

In some experiments the oxide layer on the copper powder was removed by contact with acetic acid. Copper powder (3.5 g) was added to acetic acid (1 ml, 100 ml deionized water) and heated to 70^{o}C for 24 h. The copper was then cleaned with water, acetone, 2-propanol and heptane.

Dibenzyl disulphide (DBDS) was added to the base oil (100 mg/kg) and hexadecane (350-780 mg/kg) in some experiments. Base oil was added I39 (100-200 mg/kg) in some experiments.

The total surface area of the crushed copper powder was measured using nitrogen adsorption at liquid nitrogen temperature in a Tristar II 3020 Surface Area Analyze equipment with a VacPrep 061 Degasser. The BET equation was used to calculate the surface area [23]. The surface area of the copper granules was to low to allow measurement, and was estimated by weighing individual granules and assuming dense, spherical granules. The surface area of the copper powder was estimated from the supplier information using the same assumptions.

Table 1 Overwiev of the additives used in the experiments.

	Supplier	Specifications
Copper granules	Sigma Aldrich	10-40 mesh, 9 cm^2/g (calculated)
Copper powder	Sigma Aldrich	>16 cm^2/g (calculated) (<425 µm diameter, suppliers info)
Crushed copper powder	Sigma Aldrich	4000 ± 200 cm^2/g (BET area)
Irgamet39	Ciba	Diluted in heptane, 9380 mg/kg heptane
Dibenzyl disulphide (DBDS)	Sigma Aldrich	Diluted in heptane, 10240 mg/kg heptane
Acetic acid	Sigma Aldrich	Concentrated, Water free

Table 2. Overview of the liquids used in the experiments.

Liquid	Supplier and specification	Density (g/mL)
Hexadecane	Sigma Aldrich, reagent plus, 99%	0.77
Base oil	Naphthenic oil	0.87
Uninhibited oil	Naphthenic oil, with natural antioxidants and passivators	0.88
Inhibited oil	Transformer oil, Naphthenic oil, added antioxidants and passivators	0.88
Heptane	Sigma Aldrich	0.68
Natural ester, Envirotemp ® FR3®	Cooper Power System/ Cargill	0,92

3 RESULTS

The oxidation stability of hexadecane and base oil with additives; copper, dibenzyl disulphide and the metal-passivator Irgamet39 was measured with an isothermal microcalorimeter.

To compare the oxidation stability of base oil and hexadecane the area (integral) below the micro calorimeter curves was plotted against the ratio of the sample volume over the volume of head space (air or nitrogen). This area reflects the extent of oxidation, which is an exothermal reaction, and we have previously shown that it is a measure of the stability of the liquid [18].

3.1 HEXADECANE

As seen in Figure 2 the area below curves does not increase with increasing volume of air (head space) in the same way as observations in previous experiments [18], where a clear correlation between the area below the microcalorimeter curves and the ratio between the volume of oil and volume of head space was seen. As seen in Figure 2 and Figure 3 purging with nitrogen does not have a clear effect on the area below the curve.

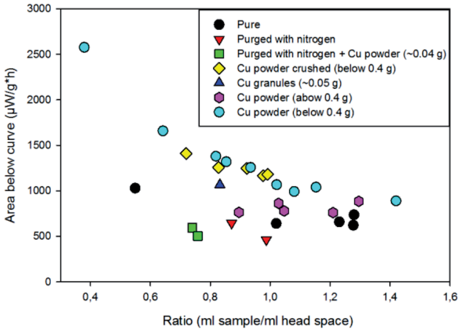

Figure 2. The area below curve (µW/g*h) for hexadecane under different conditions. Symbols: see insert in the figure. The errors were calculated to 15 %.

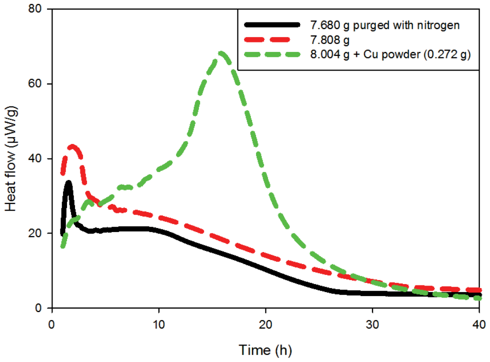

Figure 3. Microcalorimeter curves (heat flow vs. time) for hexadecane with copper powder (green dashed line) and without copper powder (red dashed line) copper powder and without copper powder purged with nitrogen (black line).

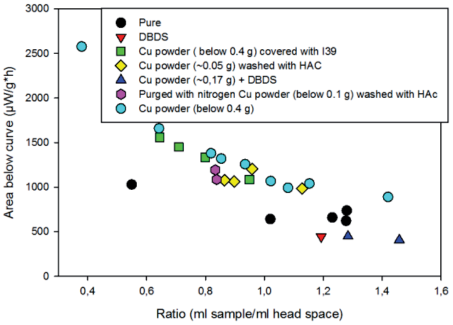

Figure 4. The area below curve (µW/g*h) for hexadecane under different conditions. Symbols: see insert in the figure. The errors were calculated to 15 %.

The effect of copper on the oxidation stability of hexadecane is presented in Figure 2-5. In Figure 3 a large peak indicates extensive oxidation between 10 and 25 hours that is not seen in the absence of copper.

From Figure 2, Figure 4 and Figure 5 it is evident that at these conditions the effect of copper depends on the amount. Low amounts (below 0.4 g) give areas larger than the area without copper. Larger amounts (more than 0.4 g) give smaller areas, values below that of hexadecane without copper added, indicating an inhibition of the oxidation.

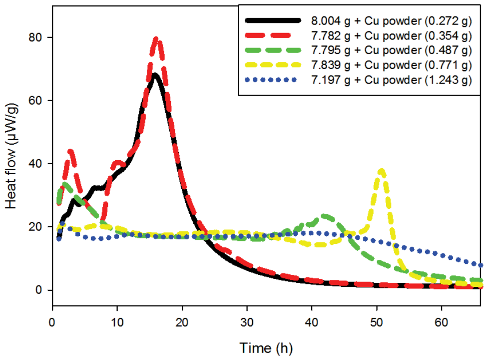

Figure 5. The microcalorimeter curves (heat flow vs. time) for hexadecane with Copper powder with varying weights (from 0.27 g to 1.24 g).

It was also observed that the peak heights decreased with increasing weight of copper as presented in Figure 5 and Figure 6.

It should be noted that the integrated area of the samples with larger weights of copper (above 0.4 g) could be slightly underestimated, since the area below the curves were measured only up to 45 h (this for practical reasons).

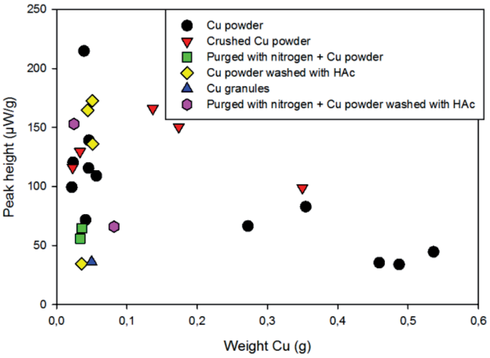

Figure 6. The peak height (µW/g) for varying weights of copper in hexadecane under different conditions (see insert for conditions).

The peaks observed for larger amounts of copper appeared after about 45 hours (Figure 5). The calorimeter curves in Figure 5 show an initial peak, with a small tendency towards shoulder between 10 and 27 hours. The initial peak could be an artifact caused by the calorimeter temperature adjustment as seen in Figure 7.

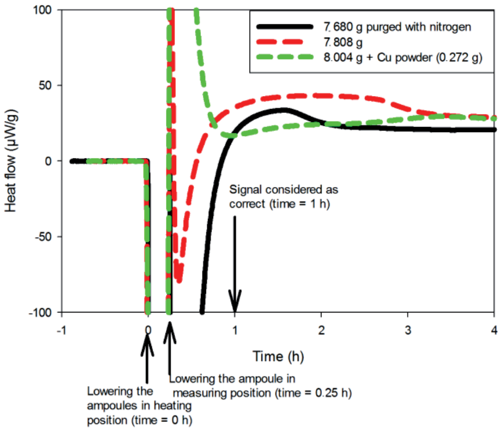

Figure 7. Initial part of the microcalorimeter curves (heat flow vs. time) with no baseline correction for hexadecane with (green dashed line) and without copper powder (red dashed line) and purged with nitrogen (black line).

The surface area of the crushed copper powder was found to be 0.4 m^2/g (BET), the surface area of the copper powder and granules was smaller and could not be measured with the available method. The crushed copper powder was found to be nonporous. The estimated surface area of the copper used is given in Table 1. The area below the curves for the samples with crushed copper is not noticeably different from the samples with copper powder with the same conditions as seen in Figure 2. When comparing the microcalorimeter curve recorded with copper granules in hexadecane with the one recorded with copper powder in hexadecane a clear difference between these two experiments is evident (Figure 8). The area below the curves for the copper granules added to hexadecane is given in Figure 2 (blue up pointing triangles), the area is smaller than for the same experiment with a small amount of copper powder (blue circles in Figure 2).

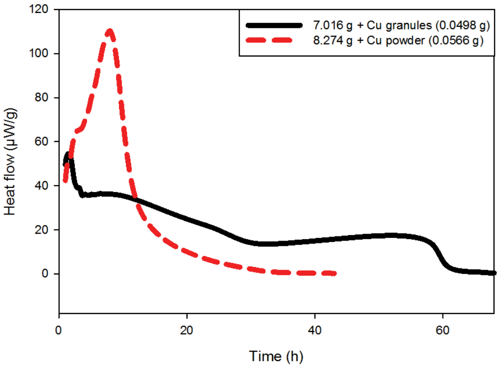

Figure 8. The microcalorimeter curve (heat flow vs. time) for hexadecane with copper powder (dashed line) and copper granules (unbroken line).

The appearance of the peak linked with the presence of copper appears to be shifted to longer reaction times with increasing weight of copper powder as in Figure 5 for copper weights above 0.4 g. The peak heights are also clearly lower as observed in Figure 6. When 1.2 g copper powder is added the peak is hardly visible (Figure 5).

The amount of oxygen was reduced in some samples by purging the liquid with nitrogen. The area below the curve is larger for the samples with air and copper compared to the samples with copper purged with nitrogen (Figure 2, blue hexagons compared to green squares) but the difference is not clear and the differences between the curves for the hexadecane purged with nitrogen and hexadecane not purged are not obvious (Figure 2). In the samples where hexadecane was purged with nitrogen and copper was added there is a clearer difference between the area under the curves compared to hexadecane with air and hexadecane purged with nitrogen (Figure 2). Furthermore the peak heights were lower when purging the samples containing copper with nitrogen as observed in Figure 6.

In order to attempt to remove the oxide layer from the copper surface, the Cu-powder was washed with acetic acid before it was added to hexadecane. The surface of the copper became brighter and the black layer on the copper disappeared after washing the copper with acetic acid as described in the experimental part. This modification of the metal did not change the area of the curves compared to the other samples with the same amount of copper as seen in Figure 4 (yellow rhomboids). But the area below the curves are larger for the samples that were purged with nitrogen and added copper washed with acid (Figure 4, pink hexagons) compared to the samples purged with nitrogen added no treated copper (Figure 2, green squares).

To look at the effect of dibenzyl disulphide (DBDS) DBDS was added to hexadecane in addition to copper. When DBDS was added to hexadecane with copper the peak that is observed with copper in hexadecane disappears as demonstrated in Figure 9.

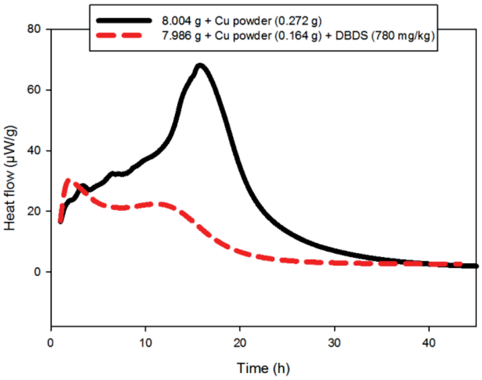

Figure 9. The microcalorimeter curve (heat flow vs. time) for hexadecane containing copper powder with (red broken line) and without (black line) DBDS

3.2 MINERAL OIL AND VEGETABLE OIL

In addition to hexadecane, mineral oils (base oil, inhibited transformer oil and uninhibited oil) and a vegetable transformer oil (ester) were used to investigate the effect of copper and additives (metal passivator and dibenzyl disulphide (DBDS)). Copper powder was added to naphthenic oil (base oil, inhibited and uninhibited) and to a vegetable oil (FR3), the specifications are given in Table 2.

The effect of the copper in base oil is seen in Figure 10 - 12.

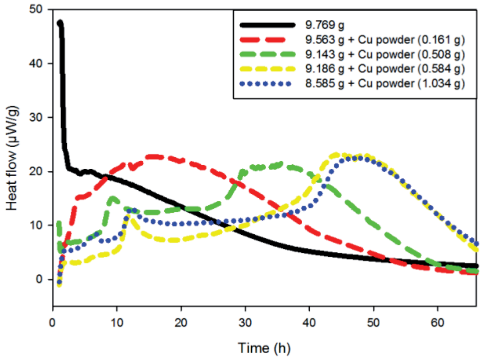

Figure 10. Microcalorimeter curve (heat flow vs. time) for base oil with different weights of added copper powder and base oil without copper (black line).

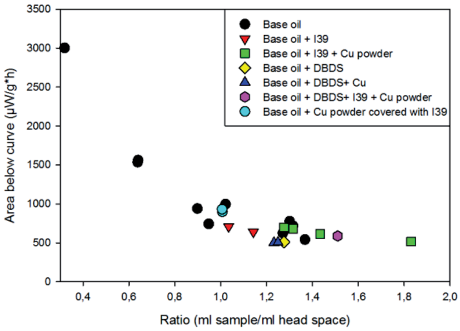

Figure 11. The area below curve vs. the ratio (up to 66 hours) between the sample volume and the volume of the head space for base oil with additives. Se insert for conditions. The error was found to be max 28 %.

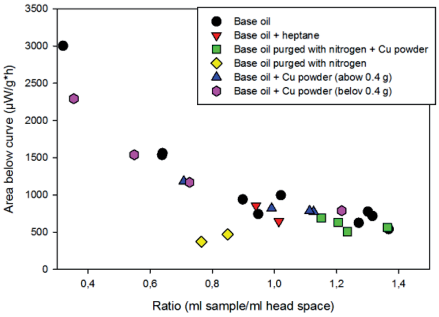

Figure 12. The area below curve vs. the ratio (up to 66 hours) between the sample volume and the volume of the head space for base oil with additives. Se insert for conditions. The error was found to be max 28 %.

The experiments with copper give a clear peak that is not seen in the oil without copper. The peak appears even after purging the oil with nitrogen as seen in Figure 13. The time before the peak appears increases with increasing amount of copper powder as seen in Figure 10.

By plotting the area of the curves (integrated after 66 h) against the ratio of the sample volume and the head space volume (Figure 11 and Figure 12) it is seen that only the base oil purged with nitrogen (pink hexagons) gives a significantly lower area than the rest of the samples with approximately the same volume of sample. There are no obvious differences between the samples with copper purged with nitrogen compared to the samples with copper not purged. Heptane does not affect the oxidation of base oil as seen in Figure 12 (red down pointing triangle).

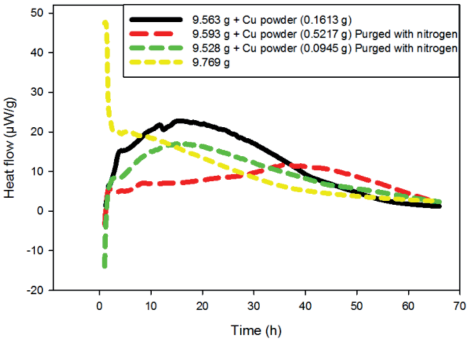

Figure 13. Microcalorimeter curves (heat flow vs. time) for base oil (yellow long dash line), base oil with copper powder (black line) and base oil with copper powder purged with nitrogen (red long dashed line and green long dotted line).

In order to investigate if vegetable-oil based liquids show the same behavior a series of experiments were performed using FR3 oil (see Table 2 for properties). Copper powder was added to the vegetable oil, in some experiments. The results of the microcalorimeter experiments are seen in Figure 14. The area below the curves is given in Figure 15. There are no significant differences between the curves with and without copper added with respect to the area below the curves.

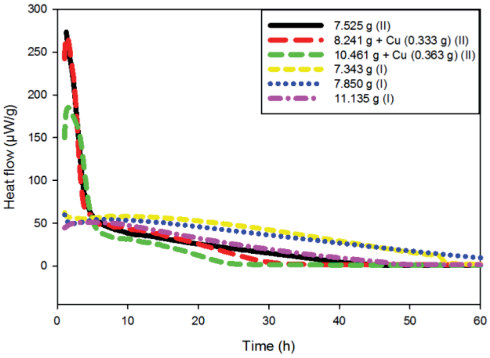

Figure 14. Microcalorimeter curve (heat flow vs. time) for the vegetable oil (ester) Envirotemp FR3 (the I and II denote different batches of the liquid).

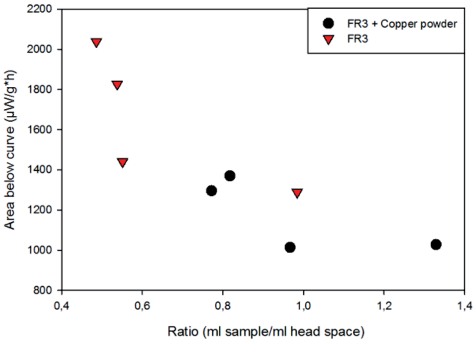

Figure 15. The area below curve vs. the ratio (up to 66 hours) between the sample volume and the volume of the head space for FR3 with (circles) and without (triangles) copper powder.

Addition of inhibitors changes the oxidation properties of the oils. Experiments with copper in uninhibited and inhibited oils were performed to investigate the combined effect of copper and the inhibitors in the oils. When comparing the microcalorimeter curves for uninhibited oil with and without copper (Figure 16) it is not possible to observe any major effect of copper in the oil. The same goes for the inhibited oil, it is not possible to conclude that there are any differences with and without copper (Figure 17). The small difference (the signal is decreasing in the start of the experiment) in the inhibited oil curves for one of the experiment (Figure 17, with added 0.4351 g copper) is probably just reflecting the uncertainty of the experiment, since the values of the heat flow are very low (max 2.5 µW/g at).

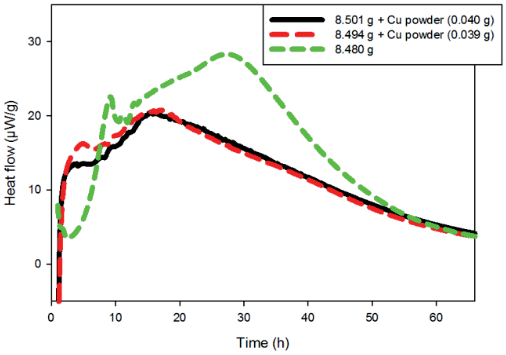

Figure 16. Microcalorimeter curve (heat flow vs. time) for the uninhibited oil with (solid line and dashed red line) and without (green dashed line) Cu powder.

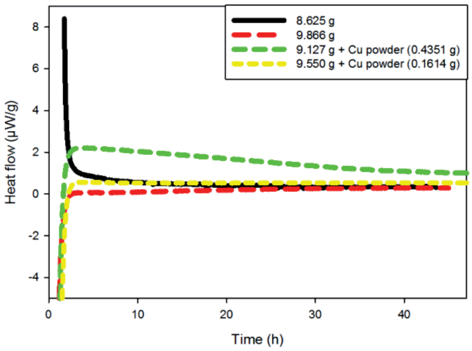

Figure 17. Microcalorimeter curve (heat flow vs. time) for the inhibited oil with copper powder (middle dashed line and short dashed line) and without copper (whole line and long dashed line).

4 DISCUSSION

It is assumed that it primarily is the oxidation of the liquid that contributes to the heat production in the system. The microcalorimeter measures the heat produced (or consumed) by the sample system, the more heat produced (exothermic reactions) the higher the measured heat flow. The calorimetric method is not specific with regard to what reactions and which components that react, but the microcalorimeter is very sensitive to the heat production.

The temperature used was chosen to be 110 °C, to facilitate comparison with earlier experiments and other ageing and oxidation study methods in transformer research [15, 18, 24].

Many of the experiments have been repeated with approximately the same amounts of liquid and additives, and as seen in the presentations of the area vs. ratio between liquid and head space the repeatability is good. As seen in Figure 2, Figure 4 and Figure 11, the area vs. ratio between volume of liquid and head space is approximately the same for experiments with the same conditions with regards to the additives.

4.1 HEXADECANE

In Figure 2 it is seen that the oxidation stability of hexadecane at 110 °C (black circles) is not dependent on the volume of the head space in the ampoule. This is different from the base oil in Figure 11 (black circles). From the experiments it is clear that hexadecane is quite stable with regards to oxidation at 110 °C when looking at the curves and the area below the curves (Figure 2 and Figure 3).

It is evident that the copper powder and the crushed copper powder contribute to and affect the oxidation of hexadecane, but the granules do not have the same effect on the oxidation. This shows that the surface area of copper is an important factor in the oxidation process. There is no difference between the crushed copper and copper powder regarding the oxidation of the hexadecane neither when comparing the area below the curves nor the curves. The oxidation is much faster and, during the first 45 hours, much more heat is produced when copper powder or crushed powder are added to the hexadecane and heated at 110 °C. This confirms the catalytic effect of copper as described in the introduction. The copper acts as a catalyst, and in order to reduce the copper-catalyzed oxidation deactivators are added to the transformer oils [25].

The area below the curve and the peak height decrease with increasing amount of copper when the weight of copper is above ~0.4 g (Figure 2 and Figure 5). This is a strange result, but has been described previously, and seems to be a result of the so-called critical phenomenon. In excess amounts copper becomes an inhibitor instead of a catalyst. On the other hand, for copper addition below 0.4 g it appears that the area and height of the peak increase with increasing weight/surface of copper, reflecting more extensive oxidation. The result corresponds to other measurements where the oxygen uptake has been measured [7, 9, 10, 12].

Washing the copper surface with acetic acid in order to remove a surface oxide layer has no effect on the oxidation of hexadecane. This is not surprising, since both copper metal and copper oxide are reported to contribute to the catalysis of the hydrocarbons [5]. However, by washing the copper with acetic acid the oxide layer is removed and cupric acetate is formed [26]. The copper ions on the surface are still available and can react with the hydrocarbons. This does not seem to change the oxidation properties.

Addition of Irgamet39 does not have a significant influence on the catalytic effect of copper. The only additive that lowers the oxidation process of hexadecane in the presence of copper is dibenzyl disulphide (DBDS). DBDS is a well-known and much used anti-oxidant in transformer liquid, and the results in Figure 9 confirm that the effect is very good. Sulphur species are also known to poison the active sites on transition metal catalyst surface [27]. However, a problem with DBDS is the formation of sulphide species and corrosion of the copper [28, 29]. This is a key issue in transformers [29]. I39 is reported to be a deactivator that forms complexes with free copper ions in the bulk solution [30]. As seen in Figure 4 and Figure 11, the I39 has not affected the oxidation of the liquids. In the samples where the I39 was chemisorbed to the copper before the copper was added to the sample the I39 was probably not accessible to the copper ions in the bulk solution. But in the samples where I39 was added as a liquid to the oil, there is no change in the effect of copper as an oxidation catalyst either. This indicates that the I39 first and foremost is an effective passivator, reducing the corrosion by sulphide species, but is less effective as an overall passivator and deactivator.

I39 is not sufficient to hinder the corrosion even if I39 has been shown as a good protector against corrosion of copper caused by sulphides in oils [29]. I39 alone is therefore insufficient as an additive for the protection of the copper. Other passivators and deactivators also have to be added to the oil.

It should be mentioned that certain oxidation products (hydroperoxides) are reported to increase the decay of I39 [31], but this effect is less likely to be of importance in the rather short experiments performed here and since the I39 was not added to the liquids but adsorbed on the copper prior to the experiments. .

4.2 MINERAL OIL AND NATURAL ESTERS

The base oil is less stable than hexadecane (comparing Figure 2 and Figure 11). For the base oil the area below the curves decreases with increasing head space ratio. This implies that the oxidation of base oil at 110 °C is dependent on the access of air. When examining closely the microcalorimeter curves for base oil (Figure 10 and Figure 14) the same effect of copper is observed in the base oil as in hexadecane; the copper increases the oxidation of the oilIt seems that the amount of copper in the system affects the oxidation more than purging the copper/oil system with nitrogen to remove oxygen, and that the effect of varying the copper amount is the same as for hexadecane where the catalytic effect of copper was evident. It also appears that the critical phenomenon is seen in the same way as in hexadecane (Figure 5). The peak with copper appears later for the larger amounts of copper.

As seen in Figure 12, after purging the base oil without copper with nitrogen (blue up pointing triangles) the oxidation is decreased comparing to the oil not being purged. However the effect of purging the oil with nitrogen decreases when copper is present in the system (yellow rhomboids). This indicates that the effect of copper is strong and the catalytic effect is large, hence there must be oxygen present in the sample even after purging with nitrogen. For the samples purged with nitrogen; the rate of oxidation is slow due to the low concentration of oxygen. When copper is present the rate of oxidation is increased due to the presence of catalyst.

The same effect of copper in transformer oil was reported previously [5, 32] where the effect of copper in transformer oil was seen as an peak in the concentration of hydroperoxide (measured with polarography) over time with solid copper present, this was not observed without copper in the sample. The soluble copper was measured, and a clear correlation between the soluble copper content and the hydro-peroxide concentration was observed. These experiments were performed at 95 ^{o}C, at 110 ^{o}C this effect is expected to be even more pronounced.

As observed in Figure 11 DBDS added to the system leads to decreased oxidation both for the system with base oil and DBDS (yellow rhomboids) and the system with base oil, DBDS and copper (blue up pointing triangles). When Irgamet39 is added in the base oil with copper and DBDS it appears that the anti-oxidant effect of DBDS is decreased (pink hexagons). A mechanism could be that the I39 is decomposed and the decomposition products contribute to the oxidation process.

Since I39 and DBDS were diluted in heptane, pure heptane was added to base oil to map the effect of heptane in the oil. No such effect was found (Figure 12, red down pointing triangles).

The areas below the curves for the vegetable oil seen in Figure 15 indicate that the oil is much more stable with regard to oxidation compared to the base oil. As seen in Figure 14 and Figure 15 the effect of copper in the vegetable oil FR3 is absent. The FR3 is a chemically modified vegetable oil and is likely to contain a mix of additives. These additives probably also deactivate the catalytic effect of copper [33]. It is also possible that the chemical composition of the liquid itself inhibits the copper. Other results have shown that ageing a commercially available natural ester, with copper added, the total acid number (TAN, that indicate oxidation) did not increase in the same way as TAN in mineral oil [34].

We did not observe any effects of copper in the uninhibited oil and the inhibited oil. In the inhibited oil the natural antioxidants and passivators present in mineral oil are removed and other passivators and antioxidants are added. In the uninhibited oil naturally occurring antioxidants and passivators are present in the oil [35]. This is probably the reason why copper does not have an observable catalytic effect on the oxidation of oil within the conditions and time lags of our studies. The passivators protect the copper from oxidation and release of copper ions into the bulk solution so there is less copper ions contributing as catalysts in the oxidation. The antioxidants also inhibit any potential oxidation catalyzed by copper ions.

The oxidation of the liquids appears to be random in terms of initiation and termination. The repeatability is good, but there are some variations in the signal during the startup. This introduces uncertainty in the calculation of the area below the curve.

Previous experiments were done using steel ampoules, in order to check for wall effects comparisons between the same experiments performed with glass cups (liners) and without glass cups were done. This showed no differences between the experiments with steel ampoules and ampoules lined with glass cups. However, the difference in the volume has to been taken into consideration.

5 CONCLUSION

An isothermal microcalorimeter has been used to investigate oxidation phenomenon in liquid dielectrics. The system was shown to be suitable to detect the catalytic effects of solid copper in oil. Hexadecane was used as model oil, and was found to be slightly less prone to oxidation compared to base oil.

The catalytic effect of copper was found to be dependent on the amount of copper added, in particular the surface area of the copper. The catalytic effect of copper was not found in the vegetable oil FR3 or in inhibited and uninhibited mineral oil. The mineral oils used here contain antioxidants and deactivators that prevent the oxidation and the catalytic effect of added copper. The critical phenomenon where copper changes from being a catalyst to acting as an inhibitor was observed when copper was added in the range between 0.3 g and 0.4 g for the copper powder used in this study. This phenomenon was also observed in the base oil.

Dibenzyl disulphide is found to be an efficient antioxidant in hexadecane and base oil, and also reduces the oxidation when copper is present in the liquid.

The metal passivator I39 does not prevent the catalytic effect of copper on the oxidation of hydrocarbon liquids.

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Ingvild Tronstad was born in Lillehammer, Norway in 1981. She is a Ph.D. degree candidate in chemical engineering at the Department of Chemical Engineering at the Norwegian University of Science and Technology (NTNU), Trondheim, Norway. She has a master degree in analytical chemistry and environmental chemistry from the Department of Chemistry, also at NTNU.

Marit-Helen Glomm Ese was born in Bergen, Norway on 21 April 1971. She received the Ph.D. degree in surface- and colloid chemistry from the University of Bergen in 1999. After several engagements as post.doc and research scientist both in USA (North Carolina State University) and Norway (Norwegian University of Science and Technology) she joined SINTEF Energy Research in 2006. Ese is working on material science for electric power apparatus. In recent years, her main focus has been towards ageing and degradation of different insulating materials (liquids, paper and polymers).

Edd Anders Blekkan was born in Steinkjer, Norway in 1957. He received the Ph.D. degree in industrial chemistry from the Norwegian Institute of Technology (NTH) in Trondheim in 1985. After a post doctoral stay in Reading, UK and a brief period in SINTEF as a research scientist in the Catalysis group he joined NTH (later NTNU) as a lecturer in 1988. He has been a full professor since 1995. His research is related to many aspects of industrial chemistry, in particular catalysis, petrochemistry, oil refining and biofuels.

Paper III

Ageing and Corrosion of Paper Insulated Copper Windings: The Effect of Irgamet39 in Aged Insulated Oil

Ingvild Tronstad, Carl Marius Roel, Wilhelm Robert Glomm and **Edd Anders Blekkan**
Norwegian University of Science and Technology (NTNU)
Department of Chemical Engineering
7491 Trondheim

and **Marit-Helen G. Ese**
SINTEF Energy Research
Department of Electric Power Technology
Sem Sælands vei 11
Trondheim

ABSTRACT

Abstract— Copper sulphide can be formed on copper windings in high voltage transformers and cause dielectric breakdown in the transformers. To avoid transformer failures caused by copper sulphide, metal passivators are added to the insulating oil. Here, the commonly used metal passivator Irgamet39 was used in combination with copper surfaces, sulphides and insulating oil in order to to investigate the effect of the passivator. Traditional methods in addition to Quartz Crystal Microbalance were used to investigate the effect of Irgamet39. It was found no effect of Irgamet39 in systems where the formation of copper sulphide had started, while the effect was found to be very good in new systems.

Index Terms — **Corrosion, dielectric breakdown, power transformers, oil insulation, Quartz Crystal Microbalance (QCM)**

1 INTRODUCTION

FAILURES in high voltage transformers have serious consequences and are therefore of large concern. Many of the failures in paper- mineral oil insulated transformers the last decades are believed to be caused by copper sulphide which deposits on the paper and weakens the dielectric strength of the insulation [3]. The sulphur may be present as a result of improper refining of the crude oil or added as sulphur-containing antioxidant molecules to the refined mineral oil. Corrosive sulphur species are defined as sulphur species that are or can become corrosive in the oil. This may be elemental sulphur, thiols, sulphides, disulphides (as dibenzyl disulphide, DBDS) and thiophenes (listed here in order of decreasing corrosivity) [4].

The sulphur species react with copper to form soluble copper sulphide species, which subsequently deposits on the paper as copper sulphide. While the mechanism of copper sulphide deposition on the paper is not fully understood, a suggested course of events to explain the process is as follows, here illustrated with DBDS as the sulphide specie [5, 6];

- DBDS-Cu dissolves into the insulating liquid
- Adsorption of DBDS-Cu onto the paper
- Decomposition of DBDS-Cu onto the paper forming Cu-S and the by-products biphenyl and dibenzene sulphide.

In these reactions free radical intermediates (denoted •) such as benzylmercaptane• and toluene• are formed. The dissolution of the copper, forming a copper-sulphur complex is affected by the temperature, with the degree of dissolution reported to be proportional to temperature [7]. The Cu-S deposit is recognized on the copper and paper as black, grey or dark brown coloured regions as seen in Figure 1 [3, 8, 9].

To replace the windings and/or the oil in a transformer is a costly initiative; therefore it is essential to develop a method to avoid the need for this since there already are transformers in service with copper sulphide attacked windings. Some issues relating to this are investigated in this communication.

Figure 1. Insulating paper with Copper-Sulphide depositions.

To prevent corrosive compounds from reacting with the copper, metal surface passivators are added to the oil. The idea is that passivators form a protecting film on the copper

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surface, providing a steric barrier protecting against corrosion of the metal caused by oxidizing compounds and corrosive sulphur species. The passivator molecules also function as a ligand, forming copper-complexes with free copper-ions in the oil. An example is Irgamet39 (I39), a tolutriazole (TTA) based molecule that is made more oil soluble through adding an N-aminomethyl group as an oleophilic "tail" (Figure 2). The passivator contains a nitrogen atom that can chemisorb onto the copper surface or react with copper-ions in the oil [10]. In the transformers, I39 is added to mineral oils in concentrations of 50 mg/kg to 200 mg/kg, typically 100 mg/kg [11-14]. When the nitrogen group in I39 reacts with the metal surface, the aminomethyl group is split off in a retro-Mannich reaction. The TTA part is left on the metal as a protecting film [11, 15]. The nature of the film is discussed in the literature, but recent findings indicate that TTA is chemisorbed onto the surface in an end-on configuration [10, 16].

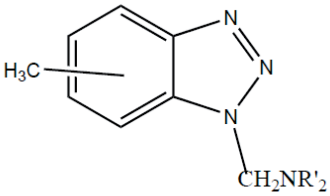


Figure 1 The structure of Irgamet39 [1]

To investigate the effect of the passivator I39 in transformers after initial formation of copper sulphide complexes, ageing experiments with and without this passivator have been performed. The passivator was added to the oil at different time of ageing. The system was studied using simple analytical tools such as potentiometric titration of the oil and visual investigation of copper and paper to study the effect on copper and oil after copper sulphide formation. It is recommended to add a passivator to the oil before use, but I39 has also been added to the oil in transformers in use, with reports indicating that the passivator works both on fresh and aged copper surfaces [11, 13].

To investigate how I39 adsorbs on copper surface, a quartz crystal microbalance with dissipation monitoring (QCM-D) has been used. Within the QCM-D instrument, a thin copper-coated quartz electrode oscillates at a fundamental frequency of 5 MHz. Upon exposing the copper surface to solutions containing potential adsorbate, adsorption can be observed as a reduction of frequency caused by an increase in the total mass of the oscillating system.

2 EXPERIMENTAL

The presentation of the experimental part describes sample preparation, ageing and analysis. All chemicals used are described in Table 1

Three main types of experiments were performed;

- Ageing of oil with Cu, paper and different concentrations of I39 and DBDS, analysed for thiols, disulphides and TAN by potentiometric titration and visual inspection of copper and paper to detect copper sulphide deposition.
- Copper Quartz crystal microbalance (QCM) analyses were used to study the adsorption of I39 on Cu
- UV-Vis spectrophotometer measurements were used to determine the concentration of I39 after different oil treatments.

The first series of ageing experiments (AE I) were done by ageing transformer oil II (Table 1) with paper covered copper conductor and I39. Unused copper windings wrapped with one or two layers of Kraft paper were cut into pieces with typical dimensions of the Cu piece 30 x 7 x 1 mm. All experiments were carried out in glass vials (75, 5 x 22, 5 mm), closed with crimp caps. An example of the copper and glass is shown in Figure 3.

Figure 2. Glass vial with a piece of copper winding wrapped with paper (one layer).

In total 112 samples with Oil II and pieces of copper with paper were prepared. I39 was added to the samples during the experiments according to the protocol shown in Table 2 and Table 3. The samples were aged at 150 ^oC between 1 and 56 days. Parallel experiments with I39 added initially were performed in order to investigate the effect of the passivator. The samples are coded as following; Samples that contained I39 are marked xDy where x is the day I39 was added to the sample and y is the sampling day. The reference samples had I39 added before ageing, and are coded as RIy where y is the day of sampling. The reference samples without I39 are marked RBy, where y also is the day of sampling. For example the sample 1D8 had I39 added after one day, and was sampled after 8 days. The reference sample RI7 had I39 added before ageing and was sampled on day 7. The reference RB7 did not contain I39 and was aged for 7 days before sampling. All the samples are also coded with "one layer" or "two layers" describing if the copper in the sample was covered with one or two layers of paper.

Table 1 Overview of the chemicals used in the experiments.

Component	Supplier	Specifications
Oil I		Naphthenic mineral oil. 0,01 mgKOH/g oil (max), conc. of sulfur max % 0,15 (information from supplier). 4±2 μgS/g oil [a]
Oil II		Naphthenic mineral oil. 0,03 mgKOH/g oil (max)(information from supplier). 32±4 μgS/g oil [a]
n-heptane (in QCM and spectrophotometric measurements)	Merck	Pro-analysis
Toluene (in QCM and spectrophotometric measurements)	Merck	AnalaR NORMAPUR
Toluene (used for cleaning of copper)	Sigma Aldrich	
White mineral oil	Sigma Aldrich	
Copper foils	Goodfellow Cambridge limited	Tickness: 0.5 mm Purity: 99.9 % Temper: Half hard
Dibenzyl disulphide (DBDS)	Aldrich	1322 mg in 200,0 ml Nytro 10XN
Irgamet39™ (I39)	Ciba	673 mg in 250,0 ml heptane
Octadecylmercaptan		70 μg/g oil, 1,000g, diluted in 30 ml 2-propanol
Zink	Sigma	
Silver nitrate	Sigma Aldirch	AgNO$_3$ in 2-propanol, 0,5mM
2-Propanol	Sigma Aldrich	
Potassium hydroxide in ethanol (KOH in EtOH)	Sigma Aldrich	0,1 M diluted to 0,02M
Copper windings with paper	From transformer manufacturer (Siemens)	Thickness : ~1 mm Kraft paper
Acetic acid	Sigma Aldrich	Concentrated, water free

[a] Measured in experiments

Table 2. Overview of the samples in ageing experiment I (AE I) with two layers of paper.

Two layers of paper			
Day of ageing before adding I39 (100 mg/kg oil)	Time of ageing before sampling (the coding of the samples is given in parenthesis)		
1	8 (1D8)	15 (1D15)	
3	9 (3D9)	17 (3D17)	31 (3D31)
7	14 (7D14)	21 (7D21)	35 (7D35)
10	17 (10D17)	24 (10D24)	
14	21 (14D21)	28 (14D28)	42 (14D42)
21	28 (21D28)	35 (21D35)	
28	35 (28D35)	42 (28D42)	56 (28D56)

Table 3. Overview of the samples in ageing experiment I (AE I) with one layer of paper.

One layer of paper			
Days of ageing before adding I39 (100 mg/kg oil)	Time of ageing before sampling (the coding of the samples is given in parenthesis)		
1	8 (1D8)	15 (1D15)	
2	9 (2D9)	16 (2D16)	
3	10 (3D10)	17 (3D17)	31(3D31)
4	11 (4D11)	18 (4D18)	
7	14 (7D14)	21 (7D21)	35 (7D35)
10	17 (10D17)	24 (10D24)	
14	21(14D21)	28 (14D28)	42 (14D42)
21	28 (21D28)	35 (21D35)	
28	35 (28D35)	42 (28D42)	56 (28D56)

In the second series of ageing experiments (AEII) varying concentrations of DBDS (0- 1000 mg/kg oil) were added to Oil I, a non-corrosive mineral oil (Table 1, 15 ml) with I39 (100 mg/kg) and to corresponding samples without I39. Varying concentrations of I39 (0- 100 mg/kg) were also added to samples with DBDS (870 mg/kg) and without DBDS. The oil samples were aged at 150 ^oC (AE II).

After ageing all the samples (AE I and AE II) were cooled, followed by removing of the oil from the paper and copper (one by one) with heptane and dried in air.

The concentration of thiols and disulphides (sulphur species) in the oil samples was measured by potentiometric titration using a combined Ag ring electrode (Metrohm), with silver nitrate as titrant. For standardization of the $AgNO_3$ solution octadecylmercaptane in white mineral oil with acetic acid (100 µL) was used. Zinc was used for the reduction of disulphide to thiols according to reaction (1)[17].

$$Zn + RSSR + 2H^+ \rightarrow 2RSH + Zn^{2+} \quad (1)$$

Some of the samples were measured 2 or more times, the mean value of these measurements is reported. The average deviation was found to be 5 % for concentrations above 10 µg S/g oil and up to 50% for concentrations below 10 µg S/g oil.

Also the total acid number (TAN) in the mineral oil was determined using potentiometric titration with potassium hydroxide as titrant and a glass electrode for measurement in non-aqueous media (Solvotrode from Metrohms). The deviation was found to be max 10 % for the values above 0.3 mg KOH/g oil and ~ 30% for values below 0.3 mg KOH/g oil.

A series of samples using non corrosive mineral oil (Oil I) and corrosive mineral oil (Oil I spiked with DBDS (300 mg/kg)), Cu and I39 was designed as described in Table 4 (ageing experiment III, AE III). The oil was aged in the same way as the other ageing experiments using glass vials closed with crimp caps, 150^oC and paper covered (one or two layers) copper conductor strips (30 x 7 x 1 mm).

All samples described above were visually characterized based on the copper and paper colour and lustre and compared with each other according to [3, 6, 18].

Quartz crystal microbalance (QCM-D) is a method based on the registration of the change in oscillation of a quartz crystal (piezoelectric) caused by physical and chemical deposition on the crystal [19, 20]. By applying an oscillating electric field across the QCM-D, an acoustic wave is induced through the crystal. By measuring the change in frequency the change in mass (Δm) per unit area can be measured [20]. Sauerbrey showed that the shift in resonance frequency is linearly dependent of the adsorbed mass (see equation 2). In equation 2, C is the Sauerbrey constant, Δm is the mass change, n is the overtone and ΔF is the frequency change [21].

$$\Delta m = \frac{C\Delta F}{n} \quad (2)$$

When the frequency is constant, the adsorption has reached equilibrium and total change of mass the crystal is obtained. An overtone (a multiple of the fundamental frequency) penetrates the substance on the crystal with different depths [22, 23]. Additional information can be extracted from the QCM-D measurements using a so called D-F plot. By plotting the change in the dissipation energy (ΔD) versus the frequency change (ΔF), the induced energy loss per coupled unit mass can be calculated. The dissipation energy is the energy lost to the environment from the crystal, a large ΔD value indicates a viscoelastic layer due to energy lost, and this could either be multiple layers or a molecule which is very large and flexible [19].

A KSV QCM Z500 from KSV Instruments ltd was used with a QSV 313 Sensor Crystal Cu 5MHZ quartz crystal, as shown in Figure 4. The active surface area is 20 mm2. The QCM-D consists of a chamber where the crystal was placed, the chamber was then filled with the solvent (1 ml), and the measurement was started when the temperature had been stable for 5 minutes. At a stable baseline (less than 1Hz drift for 5 minutes) the sample with I39 (minimum 3 ml, 100 mg/kg) was added. The adsorption studies were performed at 40 ^oC, 25 ^oC and room temperature (RT = 21-23 ^oC). Argon was used as the purge gas. One crystal was covered with DBDS; this was done by ageing the crystal in mineral oil spiked with DBDS at 130 ^oC for 5 days. Before the measurements, the crystals were rinsed with toluene, dried in air and washed with heptane before air drying again.

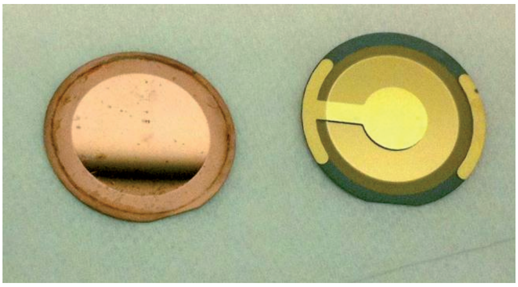


Figure 3. Quartz crystals with copper surface. The crystal to left shows the active copper surface and the crystal to the right shows the underside

Table 4. Overview of the samples in ageing experiment III (AE III)

One layer of paper, aged 24 h/ 48 h before additions			Two layers of paper, aged for 24 h before additions		
Sample (experiment number 1-6, OL=one layer of paper, 24 = 24 h ageing before exchange of oil, 48 = 48h before exchange of oil, Ref=reference sample)	Initial conditions	Conditions of exchanged oil 24 h or 48 h	Sample (experiment number 1-6, TL=two layers of paper, 24 = 24 h ageing before exchange of oil, Ref=reference sample)	Initial conditions	Conditions of exchanged oil after 48 h
1OL24 and 1OL48	Corrosive oil	No exchange, initial oil added Cu, I39 (100 mg/kg)	1TL24	Corrosive oil	No exchange, initial oil added Cu, I39 (100 mg/kg)
2OL24 and 2OL48	Corrosive oil + Cu	Fresh corrosive oil, I39 (100 mg/kg)	2TL24	Corrosive oil+ Cu	Fresh corrosive oil, I39 (100 mg/kg)
3OL24 and 3OL48	Corrosive oil+ Cu	Fresh corrosive oil	3TL24	Corrosive oil+ Cu	Fresh corrosive oil
4OL24 and 4OL48	Corrosive oil, Cu	No exchange, initial oil added I39 (100 mg/kg)	4TL24	Corrosive oil, Cu	No exchange, initial oil added I39 (100 mg/kg)
5OL24 and 5OL48	Corrosive oil, Cu	Fresh non corrosive oil, I39 (100 mg/kg)	5TL24	Corrosive oil, Cu	Fresh non corrosive oil, I39 (100 mg/kg)
6OL24 and 6OL48	Corrosive oil, Cu	No exchange	6TL24	Corrosive oil, Cu	No exchange
OLRef24 and OLRef48	Non corrosive oil + Cu	No exchange	TLRef24	Non corrosive oil + Cu	No exchange

Table 5. Overview of QCM-D experiments with I39 (100 mg/kg)

Sample	Solvent and specifications	Temperature (C°)
H1	Heptane	40
H2	Heptane	40
H3	Heptane purged with argon	RT
H4	Heptane purged with argon	RT
H/T5	50/50 wt. % heptane/toluene	40
T6	Toluene	40
H7	Heptane, the copper crystal was coated with sulphur species (aged in DBDS (1000 mg/kg))	40
H8	Heptane purged with argon, The copper crystal was coated with sulphur species (aged in DBDS (10 mg/kg))	RT
HA1	Heptane	25
HA2	Heptane	25

A fourth series of ageing experiments (AE IV) was performed in order to investigate the change in I39 concentration when ageing oil containing I39 and copper in quartz cuvettes (10 mm, from Hellma) in a UV-Vis spectrophotometer (Shimadzu UV-2401 PC), using a wavelength region of 200-600 nm. The measuring speed was set to medium and the slit width was set to 5 nm. The experiments were performed at room temperature and the calibration curve was constructed using I39 in heptane in the range 5 -100 mg/kg.

Copper foils (Table 1) were cut into coupons weighting 0.7-0.8 g, with a surface area of 350-370 mm^2. Some of the copper coupons were covered by DBDS by heating copper coupons in white mineral oil containing DBDS (10, 100, 1000 mg/kg) at 130 °C for 5 days. These copper coupons were subsequently washed with toluene and heptane and dried. The copper coupon covered with DBDS and a pure copper coupon were further aged in 3 ml heptane with I39 (100 mg/kg) at 80 °C for 5 days before the I39 concentration was measured, two copper coupons were aged in each vial.

A set of copper coupons were aged in I39 (100 mg/kg heptane) at 80°C and 90°C at 1, 2, 3, 24, 48 and 72 h in head spaced vials with crimp caps. The concentration of I39 was measured with UV-Vis spectrophotometer.

3 RESULTS AND DISCUSSION

To investigate the effect of I39 with regard to corrosion inhibition of copper surfaces, ageing experiments were performed and evaluated using potentiometric titration, QCM and UV-vis spectrophotometry.

3.1 THE CHANGE IN CONCENTRATION OF SULPHUR AND THE EFFECT OF I39

We assume that changes in the concentration of free sulphur species indicate that the sulphur is removed from the oil and either reacts with the copper or is absorbed in the paper.

The change in concentration of sulphur species in the oil aged with copper coupons and with or without I39 at 150°C (AEI in section 2) is obvious in Figure 6-8 where all the results show that the concentration of free sulphur species decreases with time when ageing the oil, with copper, at 150°C. There is no clear difference between the concentrations between one and two layers of paper, but from a visual inspection of the copper and paper it seems that the formation of copper sulphide occurs approximately one day later for the sample with two layers of paper compared to those with one layer (Table 6 row 2 and 4). As seen in Table 6, the copper-sulphide species is deposited mainly on the part of the paper that has been in contact with the edges of the copper coupons. This is also observed in [24].

As seen in Figure 4-7, the concentration of sulphur species decreases fast and stabilizes at the same value for both reference series of one and two layers of paper without I39. This indicates that the sulphur mainly reacts with the copper and is not absorbed in the paper since there is no difference between one and two layers. In the samples with I39 the concentration decreases much more slowly than without I39. Also here it seems that there is no difference with one or two layers of paper indicating that it is the copper that has an influence on the sulphide concentration, the sulphide species are not adsorbed or absorbed by the paper. The fact that the concentration of sulphur species in the oil decreases slower with I39 in the oil indicates that the I39 hinders the sulphur from reacting with the copper. As seen in Figure 4 and Figure 5 the concentration of sulphur species decreases fast if the I39 is not added before day 3. However, I39 has an effect on the concentration of sulphur if added before day three, which is also confirmed by the photos of the copper and paper (Table 6 row 1 - 8). These observations indicate that the formation kinetics of copper sulphide is slow. Moreover, the adsorption of I39 on the Cu-surface appears to be faster than the formation of copper sulphide. If the I39 is added after day three, the I39 seems to have little or no effect on the concentration of free sulphur species. Earlier studies have concluded that the formation of Cu-S starts after 72 h at 140°C [24, 25].

There is a correlation between the concentration of free sulphur in the oil sample and the corrosion of the copper in the samples as seen in Table 6 row 1 -8 and Figure 4. After 42 days (Table 6, row 8), the samples wherein I39 was added initially show indications of formation of copper sulphide in the form of black spots and small areas of lustre on the paper.

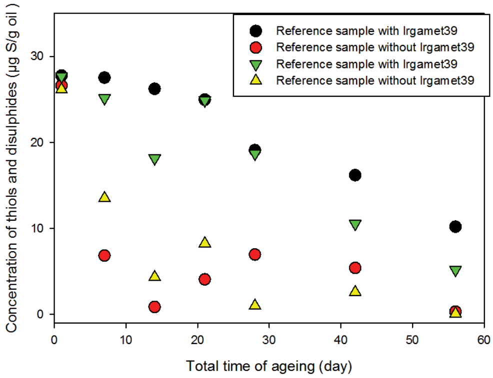


Figure 4. The concentration of sulphur species in transformer oil with copper wrapped with two layers of paper. The total time of ageing indicates the day of outtake of the samples. The series of experiments are described in section 2 (AE I) and Table 2. The deviation was found to be 5% at concentrations above 10 µg S/g oil.

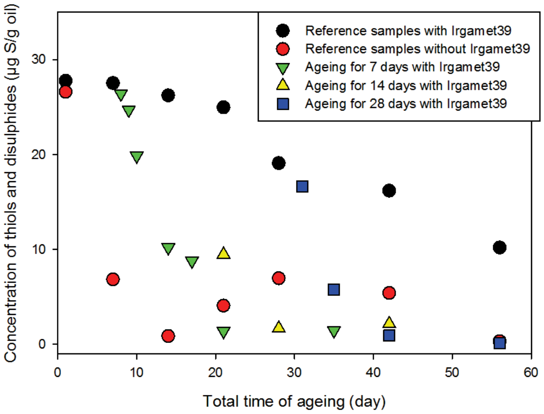


Figure 5. The concentration of sulphur species in transformer oil with copper wrapped with one layer of paper. The total time of ageing indicates the day of outtake of the samples. The series of experiments are described in section 2 (AE I) and Table 2. The deviation was found to be 5% at concentrations above 10 µg S/g oil.

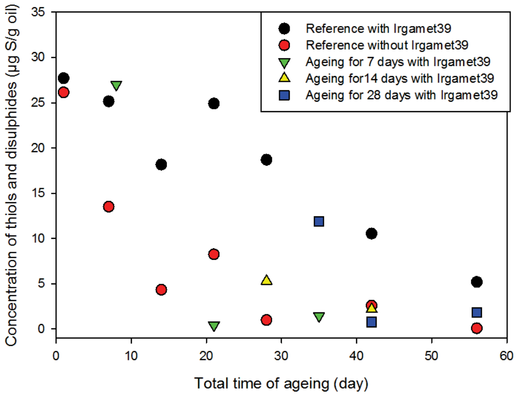
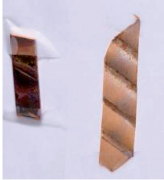
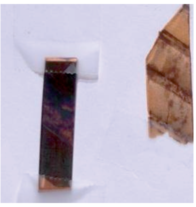
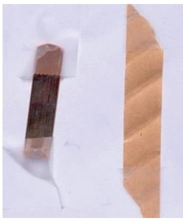
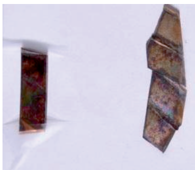
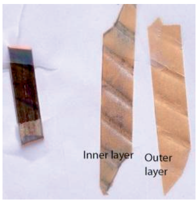
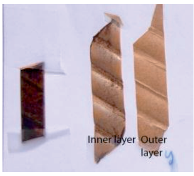
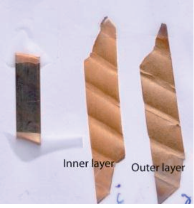
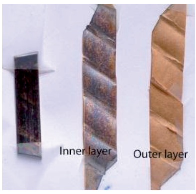
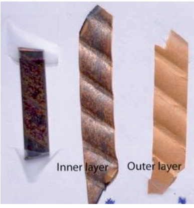
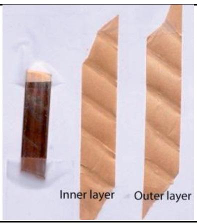
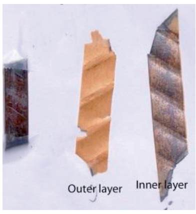


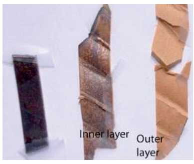
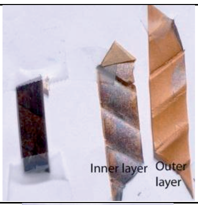
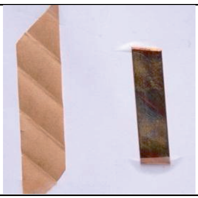
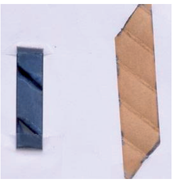
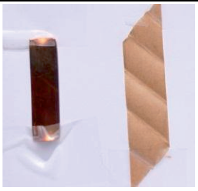
Figure 6. The concentration of sulphur species in reference samples containing I39 (with Irgamet39) and reference samples not containing I39 (without Irgamet39) . Circular symbols symbolize one layer of paper; triangle symbols symbolize two layers of paper. Time indicate the day of sampling. The deviation was found to be 5% at concentrations above 10 µg S/g oil.

The concentration of sulphur species in the samples aged with I39 present initially during the ageing is higher than the samples where the I39 were added some days into the ageing of the samples. Also, the concentration of sulphur species is higher than for the reference samples not containing I39 (without I39). Similar to the samples with one layer of paper, the concentration of sulphur species in the samples with two layers of paper also decreases with time of ageing. No correlation was found between the amount of paper in the sample and the decrease in sulphur concentration.

Varying the concentrations of DBDS (50 – 1000 mg/kg) added to oil and copper with added I39 (100 mg/kg) and ageing at 150°C for 72 h (AE II) shows that the I39 is effective up to 1000 mg/kg DBDS (Table 6 row 9 and 10). When varying the concentration of I39 and keeping the concentration of DBDS constant at 1000 mg/kg and ageing for 3 days, it is seen that only small amounts of I39 is needed to avoid formation of copper sulphide on the copper and paper. At 10 and 25 mg/kg I39 added, a formation of copper sulphide is observed, as seen in Table 6 row 10 (25 mg/kg I39) while the measured concentrations of sulphur species were found to be the same for the samples containing 10, 50 and 100 mg/kg I39. From these observations it seems that the more than 25 mg/kg I39 is enough to prevent formation of copper sulphide at 150 °C for 72 h. This experiment was performed by adding I39 at the start of the experiment.

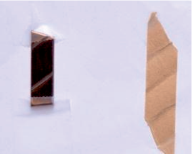
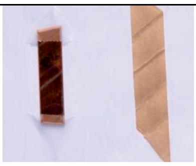
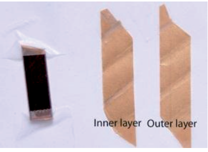
Table 6 Pictures of a selection of copper and paper samples from ageing experiment I and II. The coding is described in section 2 and Table 2 and 3.

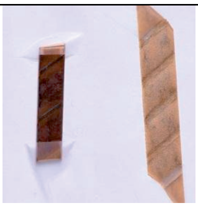
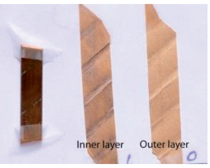
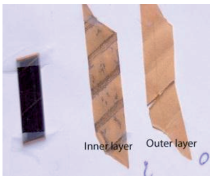
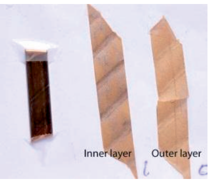
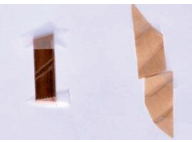
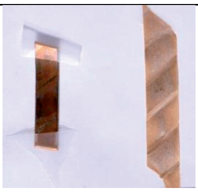
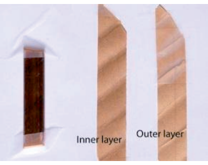
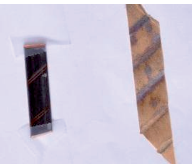
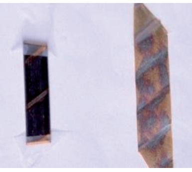
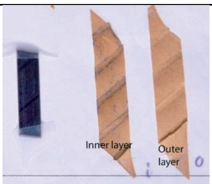
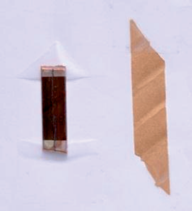
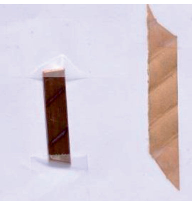
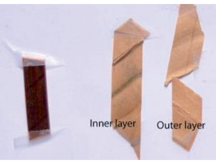
Row	Picture	Description	Picture	Description	Picture	Description
1		2D9 One layer		RID9 One layer		RBD9 One layer
2		3D10 One layer		RI 39 D3 One layer		RB D3 one layer
3		3D17 One layer		3D31 One layer		RB D17 One layer
4		3D10 Two layers				RB D3 Two layers
5		3D17 Two layers		RI39 D17 Two layers		RB D17 two layers
6		7D14 Two layers		RI39 D7 Two layers		RB D7 Two layers

Row	Picture	Description	Picture	Description	Picture	Description
7		7D21 Two layers				RBD14 Two layers
8				RI39 D42 Two layers		RB D42 Two layers
9		1000 mg/kg DBDS, 100 mg/kg I39		1000 mg/kg DBDS, 0 mg/kg I39		0 mg/kg DBDS, 0 mg/kg I39
10				1000 mg/kg DBDS, 50 mg/kg I39		1000 mg/kg DBDS, 25 mg/kg I39

To investigate whether aged oil affects the influences of I39, a series of samples using corrosive oil, non-corrosive oil, I39 and Cu was prepared as described in section 2 (AE III, Table 4). The pictures of the samples are presented in Table 7 row 1 -7. It can be seen that Cu is more attacked when the corrosive oil is changed to a fresh corrosive oil after 24/48 h, as seen in sample 3 (row 3), but the paper is more attacked when the corrosive oil is not exchanged after 24h/48h as seen in sample 6 (Table 7, row 6) . For sample 2 where corrosive oil was added initially and the corrosive oil was replaced and I39 added after 24 h (2OL24, 2TL24, row 2) there is no differences from the sample 4 that was aged with corrosive oil initially and I39 was added after 24 h (4OL24 and 4TL24, row 4). There is no difference if I39 is added to new corrosive oil or aged corrosive oil. This indicates that the products in the oil formed during the ageing of oil for 24 h do not increase the negative effect on the inhibiting function of I39 on the protection of the copper compared to fresh corrosive oil. . However, when ageing the copper coupon in corrosive oil for 48 h before replace the oil with a fresh corrosive oil containing I39 (2OL48, row 2) there is a clear difference between this sample and the sample where the copper in corrosive oil aged for 48 h is added I39 without replacing the oil (4OL48, row 4). This indicates that I39 has lost some effect, or the ability to protect the copper is weakened by the ageing products in the oil. It can also be inferred that the copper-sulphide layer on the copper surface hinders the I39 from protecting the copper.

Table 7 Pictures of a selection of copper and paper samples from ageing experiment III. The coding is described in Table 4.

Row	Picture	Description	Picture	Description	Picture	Description
1		1 OL 24		1 OL 48		1 TL 48

2	 2 OL 24	 2 OL 48	 2 Tl 48
3	 3 OL 24	 3 OL 48	 3 TL 48
4	 4 OL 24	 4 OL 48	 4 TL 48
5	 5 OL 24	 5 OL 48	 5 TL 48
6	 6 OL 24	 6 OL 48	 6 TL 48
7	 Ref OL 24	 Ref OL 48	 Ref TL 48

In sample 3 where the corrosive oil that was used initially was replaced with fresh corrosive oil after 24 or 48 h, there are only small differences between the sample where the oil was changed after 24h (3OL24, row 3) and 48 h (3OL48, row 3) when examining the paper, but there is a larger difference between the copper coupons in these samples. This may indicate that the formation of copper-sulphide on the paper is quite slow.

When comparing the samples where the corrosive oil was replaced with a fresh batch of corrosive oil containing I39 (sample 2) with the samples where the corrosive oil was replaced with non-corrosive oil containing I39 (sample 5), as expected we find that sample 5 (exposed to non-corrosive oil) is less corroded than sample 2 (row 2) which has been exposed to corrosive oil through the experiment. There is a clear effect of replacing the corrosive oil with oil a non-corrosive one but the I39 does not remove the copper-sulphide already formed.

The samples where the corrosive oil was neither replaced, nor contained I39 (sample 6, row 6) the paper is more attacked by sulphide in the sample with one layer (6OL48) compared to the sample with two layers of paper (6TL48). This indicates that the copper sulphide species are diffusing to the outer layers of paper and conductive copper sulphide distribute through the paper layers and causing flashover. The copper coupons aged for 48+48 h are as expected more corroded than the samples aged for 24+48 h.

3.3 THE CHANGE IN TOTAL ACID NUMBER

Acidity is an important parameter in mineral oil analysis. The acidity resulting from degradation of the oil weakens the dielectric effect of the oil. Therefore the total acid number (TAN) was measured to investigate whether I39 affects the formation of acids in the oil. As shown Figure 8 there is no discernible effect of I39 on the TAN. Both with and without I39 the TAN increases with time of ageing. This correlation was found for all the samples studied here with respect to time of ageing and TAN. It may seem that the formation of acid initially follows a linear trend, up to about 25 days, when the production of acids seems to level off. This may be because the oxygen in the vials is consumed so that the oxidation reactions are slowed down. The results indicate that the TAN is independent of the addition of I39. No systematic difference between the samples with one or two layers of paper with regard to the acid number was observed.

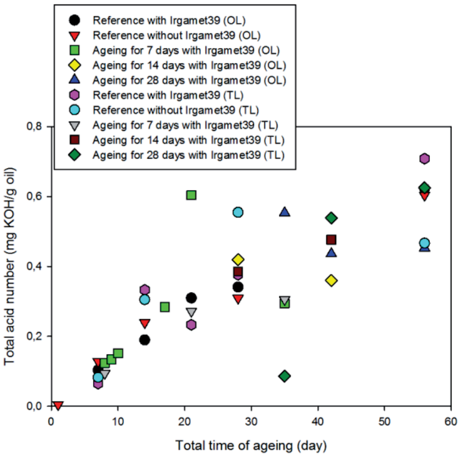


Figure 7. The change in total acid number (mg KOH/g oil) after ageing at 150 °C in between 1 and 56 days with or without I39 (100 mg/kg oil). OL is indicating one layer of paper and TL indicates two layers of paper. The series of experiments are described in section 2 (AE I), Table 2 and Table 3. The deviation was found to be 10 % for the values above 0.3 mg KOH/g oil and ~ 30% for values below 0.3 mg KOH/g oil

In the experiments where DBDS and I39 were added to the oil which then was aged as described in section 2, AEII, varying the DBDS concentrations with or without I39 addition does not give any differences in the measured TAN, indicating that disulphides together with I39 do not affect the formation of acids in the oil. This indicates that I39 does not affect the oxidation of the oil or decompose into acidic products in the oil, and that addition of I39 in these concentrations (100 mg/kg) to the oil will not cause problems with regards to the acidity. Other studies have showed that oils with I39 form more gases under thermal stress than oils without [26, 27]. This experiment was performed with oil I that is an inhibited oil containing anti-oxidants that may be the reason that the I39 and DBDS does not give any change in the TAN.

3.4 ADSORPTION OF IRGAMET 39 ON COPPER

To investigate the mechanism of I39 adsorption on copper and monitor the amount of I39 adsorbed onto copper, a Quartz Crystal Microbalance with dissipation monitoring (QCM-D) was used. The QCM-D chamber was filled with I39 (in heptane), the change in the frequency of the oscillation on the copper crystal was measured, and the change in weight on the crystal was calculated using the Sauerbrey equation. **Figure** 8 and Figure 9 illustrate how the QCM-D results are interpreted. Using the Sauerbrey equation (1, in section 2) and assuming that there is a full monolayer coverage at the break in the frequency change vs. time plot, the adsorbed mass per cm^2 of I39 or TTA onto copper was calculated (Table 8). Also the delta D vs. delta frequency plot provides information about the kinetic regimes involved in adsorption. The end of monolayer coverage, i.e.; saturation beyond monolayer coverage is followed by changes in the dissipated energy per unit frequency change (transition from rigid monolayer to a more flexible monolayer) as illustrated in Figure 8.

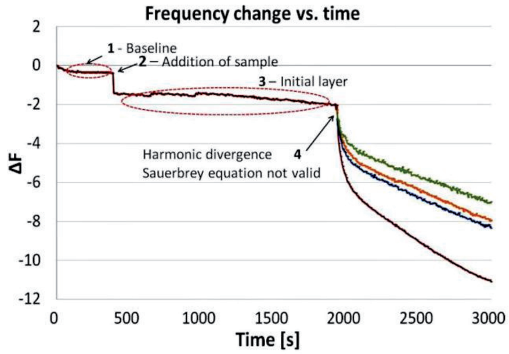


Figure 8 Delta frequency change vs. time plot illustration of the different physical characteristics of QCM-D adsorption. The first plateau (1) is the baseline, the frequency of the solvent and used as the reference for this experiment. The time used to achieve the baseline is short compared to the time of the rest of the experiment so the baseline is hardly visible in the plots of the experiments. The first break (2) in the frequency change vs. time plot is the addition of the sample. Next plateau (3) is the initial layer or monolayer. (4) Is assumed to be where the monolayer coverage is completed. After point 4 (more to right) the overtones divergences, indicating that a multilayer adsorption and leading to inaccuracy when using the Sauerbrey equation.

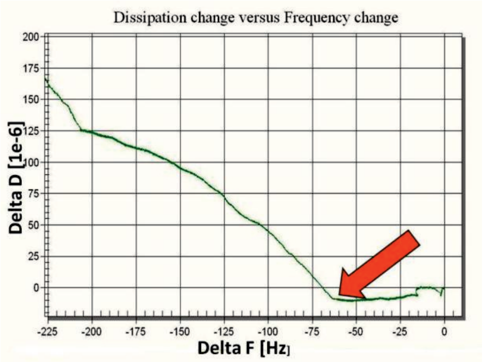


Figure 9 D-f plot of the 3 rd. overtone (harmonic) of sample 3, Irgamet 39 (100 mg/kg in heptane, deoxygenated). The arrow indicates a change in regime (the end of monolayer coverage).

From the molecular weights of TTA and I39 a rough estimate of the surface area of the adsorbing molecules can be calculated. This calculation is done based on the assumption of monolayer coverage. The Sauerbrey model was used despite the multilayer cover of the surface to calculate the saturated mass adsorbed; at saturation this is a rough estimate, but at the very least a measure of relative mass changes between systems. The results of the calculations are given in Table 8. The adsorbed mass of both I39 and TTA is calculated since the aminomethyl group ("tail") is detached from the aromatic core ("head") of the I39 before reaching complete monolayer coverage as mentioned in section 1.

As seen in Table 8 the weight of the adsorbed monolayer is lower when toluene is used as solvent, also when a mix of heptane and toluene is used the weight of the mass adsorbed on the crystal is lower than the mass adsorbed in heptane. This result is supported by the Hildebrandt solubility parameters of the solvents and I39. The difference between the solubility parameter of toluene and I39 (δ_{I39}- $\delta_{toluene}$= 0,3) is smaller than the difference between heptane and I39(δ_{I39}- $\delta_{heptane}$= -1,08) [28]. This means that I39 is more soluble in toluene than in heptane. The solubility of I39 is lower in the mixed solvent than in the pure toluene. The area per molecule is calculated to be larger in toluene; the I39 is more solvated in toluene than in heptane, giving a larger area per molecule. It seems also that the transition from monolayer to multilayers is less well-defined in toluene than in heptane. This makes it more difficult to ascertain where the transition to multilayer occurs. From our results, it may be a correlation between the type of solvent and the rate of adsorption, as formation of monolayer was found to occur slower in toluene than in heptane. It seems then that the aminomethyl group on I39, that is making it more soluble in the oil, is slowing the adsorption process on copper, but it also seems that the formation of copper sulphide is so slow that this will not be a problem.

The value |ΔD/ΔF| represents the value for the change of dissipation over frequency change and provides an indication of the relative rigidity if the adsorbed layer. A high | ΔD/ΔF| means that the adsorbed layer is less rigid. This agrees with the theory that toluene is a better solvent and therefor gives a more rigid layer than heptane and that more molecules are adsorbed on the surface in heptane as shown in Table 8 (samples H/T5 and T6).

The I39 still has an effect when added two days after the onset of ageing in corrosive oil as seen in Figure 4, Figure 5 and Table 6. From the results in Table 8 it seems that higher temperatures result in faster monolayer coverage. The estimated area of TTA is 1.31 nm^2 /molecule, and 3.4 nm^2 /molecule for I39, respectively.

It has been proposed that the BTA-molecules chemically bond to the metal or metal-oxide and orient parallel to the surface, creating a BTA- copper film with polymeric structure and a film thickness lower than 50 Å (Cotton and Scholes, 1967). Calculations done by Jiang and Adams (2003) however indicate that the BTA ions orients themselves perpendicular or with a tilting angle to the surface [29-31]. The results from the calculations of the area of the molecules that cover the copper surface as a rigid layer from the QCM results indicate that the molecules either are adsorbed in a side-on stacked orientation or orientated end-on (Figure 11 right side). The rigidity of the adsorbed layer indicates that the molecules are close to each other.

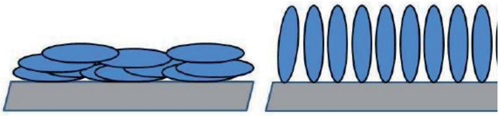


Figure 10 Sketches of possible orientations of the I39/TTA molecule. The left shows a side on orientation- stacked and the right shows an end on orientation. From [2]

Figure 10 reveals the D-f plot of a QCM-D experiment with I39 (100 mg/kg in heptane) performed at room temperature (H3). The arrows indicate possible regime shifts; the first arrow from the right (start) indicates a shift from a rigid regime to a more visco-elastic regime; this break is used for indicating the end of the monolayer. When multilayers are formed, changes in the adsorption regimes could be due to changes in the configuration, indicating either a closer packing of molecules or a looser molecule bonding. The next arrows (to the left) signify regimes that are harder to interpret, and indicate that the adsorption goes through many kinetic regimes and that unknown factors influence the rate of adsorption. This can explain the large variations observed in the time of the formation of monolayer and saturation.

Table 8. Results of the QCM experiments; calculated mass at monolayer coverage, time at monolayer coverage, calculated molecular area of I39 at the surface and the adsorbed mass at saturation.

Sample	Time (h)	Monolayer mass (ng/cm^2)	Molecular surface area TTA (nm^2/molecule)	Molecular surface area I39 (nm^2/molecule)	ΔD/ΔF	Saturated adsorption mass (ng/cm^2)
H1 (40°C)	6.5	463±70	0.048	0.139	24.4	2322±710
H3 (RT) purged with argon	15.3	728±15	0.031	0.088	14.6	8615±1895
H4 (RT) purged with argon	13.2	1563±41	0.015	0.041	17.8	3656±407
H/T5 (40°C)	4.2	245±16	0.091	0.262	6.0	
T6 (40°C)	9.0	211±73	0.105	0.304	6.7	
HA1 (25°C)	7.8	1086±12	0.020	0.059	22.2	4340±516
HA2 (25°C)	2.1	1106±46	0.020	0.058	17.8	2760±758

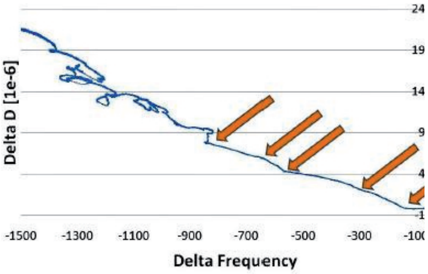


Figure 11. D-f plot of experiment H3, the arrows indicate changes in different adsorption regimes. From [2]

In the experiment where the crystal was covered with sulphide as described in section 2 (H8), the initial part of the graph shows a large mass change (Figure 13) from 0 to 5000 sec. This may be due to solvation of the sulphide layer that covers the crystal surface. The solvent (heptane) could arrange between the sulphide molecules that covers the surface (solvating the sulphides). This will affect the frequency change and be registered as increased mass and increased viscoelasticity at the surface of the crystal.

The sulphide layer on the crystal results in a less rigid system, seen as dissipation in the harmonics. The base line is less rigid for the crystal covered with sulphide than the base line for the clean crystals. Because of the assumptions that have to be made when using the Sauerbrey equation, the resulting calculations provide only an approximation of the mass adsorbed on the surface at the steady state condition. This mass was in experiment H8 calculated to be 2108 ± 324 mg/cm2. The fact that mass changes are observed indicates that I39 adsorbs on the surface even if the copper is covered with sulphur. This is also shown in the results (Table 9) from the experiments where the copper coupons was aged in DBDS (10, 100 and 1000 mg/kg oil) and thereafter in I39 (100 mg/kg heptane) to 80 °C in 72 h. The concentration of I39, measured with UV-Vis spectrophotometry, is lower in the samples where the copper was covered of DBDS in the concentrations of 100 and 1000 mg/kg. The samples that was covered with so large concentrations of DBDS was so corroded that the copper-sulphide layer started to flake of. But it is seen in the sample where the copper coupon was covered with DBDS in the 10 mg/kg solution also had a lower concentration of I39 than the samples with the copper coupon not covered with sulphide. The fact that the copper sulphide layer started to flake of may be the explanation of the large difference in the concentration of I39 due to a larger area on the copper coupons.

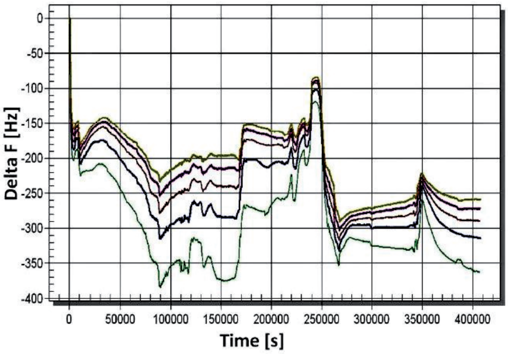


Figure 12 Delta frequency change vs. time plot for experiment H8 with copper coated with sulphide species. The different curves illustrate the different overtones (the curve that has the lowest value is the third overtone and the topmost curve is the eleventh overtone).

Table 9. The change of the concentration of I39 in addition of copper coupons covered with Cu-DBDS. The concentration was measured with UV-Vis spectrophotometry.

Concentration of DBDS (mg/kg) in the oil where the copper coupons were aged at 150°C in 72h.	Concentration of I39 (mg/kg heptane)	Concentration of I39 per g copper (mg I39/kg heptane)/g Cu
0	100,5 ± 0,5	44 ± 2,6
10	98,6 ± 0,9	39 ± 5,4
100	70,7 ± 4,6	31 ± 5,9
1000	63,3 ± 8,4	24 ± 4,4

By measuring the concentration after ageing copper pieces in heptane with I39 it is observed in Figure 13 that the concentration of I39 decreases with time and that the concentration of I39 decreases faster at 90°C than 80°C.

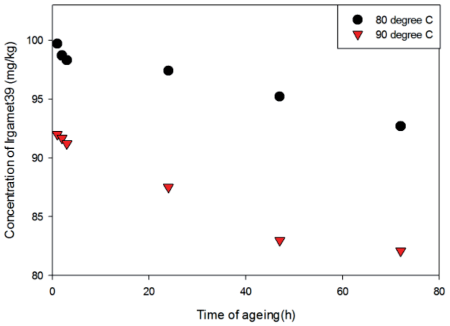


Figure 13. The change in concentration of I39 with time at 80°C (black circles) and 90°C (red triangles) measured with UV-Vis spectrophotometer.

UV-Vis spectrophotometry was used to monitor the change in I39 concentration that is believed to be caused by adsorption on copper surface. I39 was measured in heptane in a quartz cuvette using a monochromatic light in the range of 200-600 nm. The ageing experiments IV (AE IV) with sulphide covered copper was performed as described in section 2. When measuring I39 concentration with UV-Vis spectrophotometer, a shift in the absorption wavelength was observed for higher I39 concentrations. The concentrations from 1-20 mg/kg of I39 were measured at 273 nm while the concentrations of I39 from 20 to 100 mg/kg were measured at 281 nm. This may be explained by the release of the aminomethyl group "tail" under adhesion to copper.

The aminomethyl group contains an imine group which is absorbing light at a wavelength near the wavelength at which I39 absorbs. When the surface is covered by a monolayer of I39, the chemisorption of I39 begins and indicates that the aminomethyl group is lost from the aromatic core of the I39 molecule.

4 CONLUSION

By ageing corrosive mineral oil with pieces of copper and addition of I39 in different concentrations and after different ageing time it is observed that the concentration of sulphur species in the oil decreases with time if I39 is not added to the oil before ageing at 150 °C. The effect of I39 is good provided the passivator is added to the oil before use in concentrations above 25 mg/kg oil. The temperature affects the amount of adsorbed I39. The I39 seems to adsorb on the copper also after formation of copper sulphide, but the effect of I39 as a metal passivator is reduced. The I39 does not affect the formation of acids in the oil. I39 is an efficient metal passivator if added to the transformer oil before use, and may have a small effect if added early in the transformers life; if the formation of copper sulphide is severe the effect of I39 is weak.

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Ingvild Tronstad was born in Lillehammer, Norway in 1981. She is a Ph.D. degree candidate in chemical engineering at the Department of Chemical Engineering at the Norwegian University of Science and Technology (NTNU), Trondheim, Norway. She has a master degree in analytical chemistry and environmental chemistry from the Department of Chemistry, also at NTNU.

Marit-Helen Glomm Ese was born in Bergen, Norway on 21 April 1971. She received the Ph.D. degree in surface- and colloid chemistry from the University of Bergen in 1999. After several engagements as post.doc and research scientist both in USA (North Carolina State University) and Norway (Norwegian University of Science and Technology) she joined SINTEF Energy Research in 2006. Ese is working on material science for electric power apparatus. In recent years, her main focus has been towards ageing and degradation of different insulating materials (liquids, paper and polymers).

Edd Anders Blekkan was born in Steinkjer, Norway in 1957. He received the Ph.D. degree in industrial chemistry from the Norwegian Institute of Technology (NTH) in Trondheim in 1985. After a post doctoral stay in Reading, UK and a brief period in SINTEF as a research scientist in the Catalysis group he joined NTH (later NTNU) as a lecturer in 1988. He has been a full professor since 1995. His research is related to many aspects of industrial chemistry, in particular catalysis, petrochemistry, oil refining and biofuels.