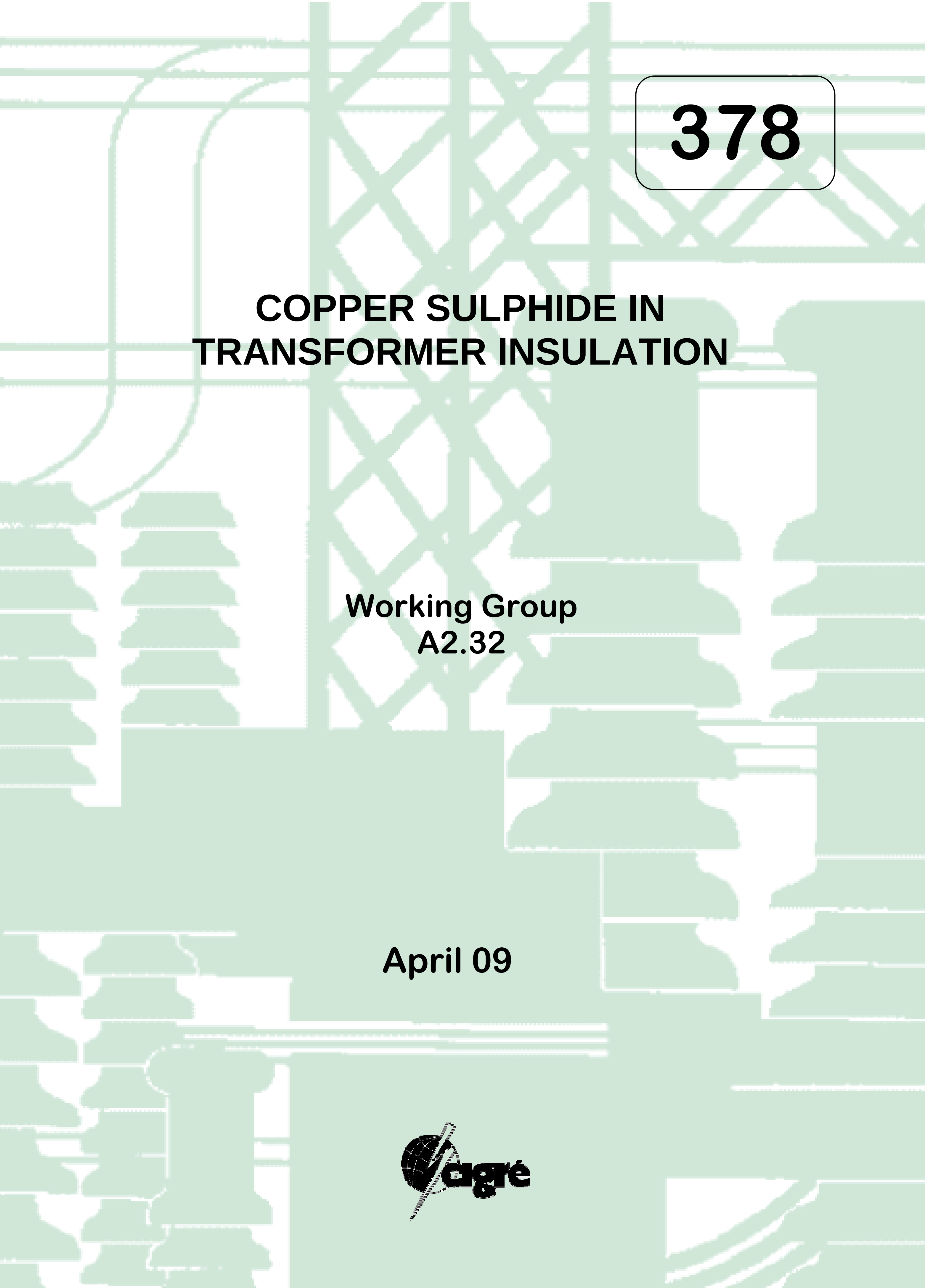

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COPPER SULPHIDE IN TRANSFORMER INSULATION

Working Group
A2.32

April 09

CIGRE WG A2.32

Copper sulphide in transformer insulation

MEMBERS:

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K. Sundkvist, Sweden
J. Van Peteghem, Belgium

CORRESPONDING MEMBERS:

X. Chendong, China
Y. Vachiratarapadorn, Thailand

FORMER MEMBERS:

V. Null, Germany
V. Sokolov, Ukraine†
Eric Sandré, France

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1 Introduction

WG A2-32 was set up in 2005 to deal with the problem of the formation of copper sulphide (Cu_2S) in transformer insulation.[1] This phenomenon has caused numerous failures in transformers and reactors. Even though it has only relatively recently been recognized as a serious problem, the re-examination of old failure cases indicates that the problem is not new. However, there is little doubt it has been increasing in recent years. The full extent of problems due to copper sulphide formation in the insulation are still not mapped in great detail. An attempt by this WG to gather information by distributing a questionnaire to equipment operators has been only partly successful. In terms of applications identified as affected, at least initially, most failures were with shunt reactors, generator transformers, and HVDC converters. However, other applications for which there are official reports (or at least failures known to the WG members) include industrial rectifiers, traction line feeders and large distribution transformers. In terms of the number of copper sulphide related failures, the statistics are even less reliable. Estimates from different parties vary widely. It seems that only a small proportion of all cases have been officially reported, or submitted for inclusion in the questionnaire conducted by A2-32. On the other hand, copper sulphide is found in many transformers when dismantled after failures, also those that failed for other reasons. It is possible that some failures have been falsely attributed to copper sulphide. However, this WG estimates that the total number of failure cases since 2000 may be in the region of 100, not counting transformers too small for any failure investigation to be carried out.

As indicated above, the reply rate to the questionaire has been very low, and therefore most conclusions in this report are based on other sources of information. The publication of this report may stimulate the interest to report cases. For this reason the questionaire will be maintained on the SC A2 web site, for the benefit of future working bodies in this area.

Problems with copper sulphide formation are not necessarily limited to contamination of the winding insulation, other potential problem areas are bushings and tap changers. The existence of copper sulphide particles in oil has also recently started to gain attention. However, these issues are all outside the scope of this working group. They may become the subjects of new working bodies, if there appear reports of extensive problems. Neither does this WG deal with the contamination of transformer insulation by conductive oil degradation products in general. Its terms of reference dictate that its scope is to deal with oil testing and specification issues, find methods to identify units in danger, give recommendations for counter-measures, and to strive for an improved understanding of the whole complex problem related to the formation of copper sulphide in cellulosic insulation.

This is the final report of WG A2-32, and marks the conclusion of the work of this particular CIGRE working body. However, it is anticipated that plenty of research and new developments will occur in this area in the future, both in understanding of the mechanisms of sulphide formation and the failures, but also in mitigation techniques. This WG could have carried on indefinitely gathering information and waiting for more research results, but it is prudent to draw the line somewhere. Maintaining the original time plan, and summarising the state of the art knowledge at this point in time, seems the most sensible thing to do.

2 The phenomenon

Since the problem started to gain attention in the first years of the 21st century [2, 3], there have been many observations of copper sulphide. One striking feature of this phenomenon is the multitude of different appearances the sulphide deposits may have. Fig. 1 shows some examples from real-life observations.

Fig 1a Discolouration of copper conductors from a failed shunt reactor, from [24]

Fig. 1b Contaminated covering paper, note the dark colour easily mistaken for sludge, from [24]

Fig.1c Area of breakdown, seen from top, from [24]

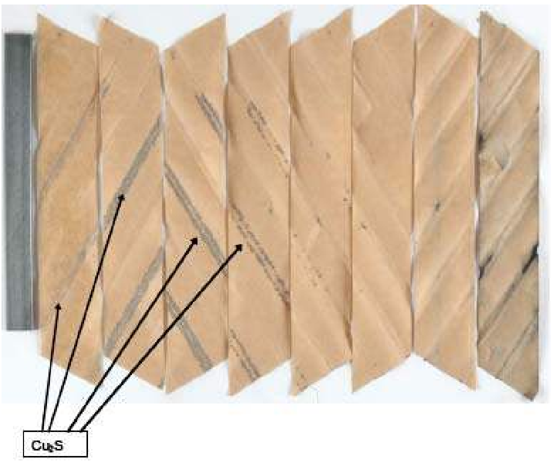

Fig. 1d Copper sulphide deposits in different paper layers (conductor from a failed GSU)

Fig. 1e Copper sulphide deposits found under spacer in failed HVDC transformer, from [18]

Fig. 1f Conductor and papers from the inspection of a failed unit

Fig 1g Copper sulphide formation on heavily aged papers from a failed industrial transformer.

Fig 1h Formation of copper sulphide on leads in 20/30kV industrial transformer. from [4]

2.1 Copper sulphide formation

2.1.1 Mechanism

So far little has been published on the mechanism of copper sulphide formation in the literature. The oil has been found to play a predominant role, being a source of sulphur compounds able to react with copper.[4, 5] Oils containing reactive sulphur species, identified in most cases as dibenzyl disulphide (DBDS), can react with copper to form copper sulphide on the surface of the conductors and on the paper insulation surfaces, even under the normal operating conditions of the transformer. However, it is far from obvious how copper can be transported into the layers of covering paper, or onto cellulose surfaces facing the oil. There has been speculation about mercaptans [18] and H_2S [6] as reactive sulphur intermediates able to carry copper, and it has also been proposed that copper sulphide is formed at the copper surface by direct reaction between copper and sulphur compounds [7, 24] and then transported as copper sulphide into the paper where it is then deposited. Scant support has been given so far for any of these theories.

Only recently has a more comprehensive model been presented. [8, 9] This model proposes that copper sulphide is formed via a two-step reaction. In the first step, oil-soluble complexes containing copper and one particular disulphide (*viz*. dibenzyl disulphide; DBDS) are formed. The oil-soluble complexes diffuse through the insulating oil and can adsorb on the paper or board matrix. In the second step, the complexes are decomposed and copper sulphide is formed, as shown in Fig. 2. This mechanism was proposed on the basis of quantitative experiments, in which a clear correlation between weight change of copper strip and decrease of DBDS concentration was found. At low temperatures, the weight of copper strip decreases because the formation rate of complexes is higher than their decomposition rate. While at high temperatures, the weight of the copper strip increases because the decomposition rate is higher than the complex formation rate. The temperature where the decomposition becomes predominant (*i.e.* faster than dissolution) is about 150 ºC in oxygen-poor conditions. Moreover, this model proposes that dibenzyl sulphide (DBS) and bisbenzyl (BiBZ) will be formed in insulating oil as by-products of copper sulphide formation between copper and DBDS. In laboratory experiments, it is confirmed that these by-products are found in oils. Montoring the production of these by-products or the decline of DBDS content could provide a diagnostic method to estimate the total amount of copper sulphide in transformers (though no conclusions should be based only on this information, since these changes could be due to other processes). This model is so far the only one presented with a firm foundation in quantitative experiments. The model can also be easily expanded to other similar sulphur species.

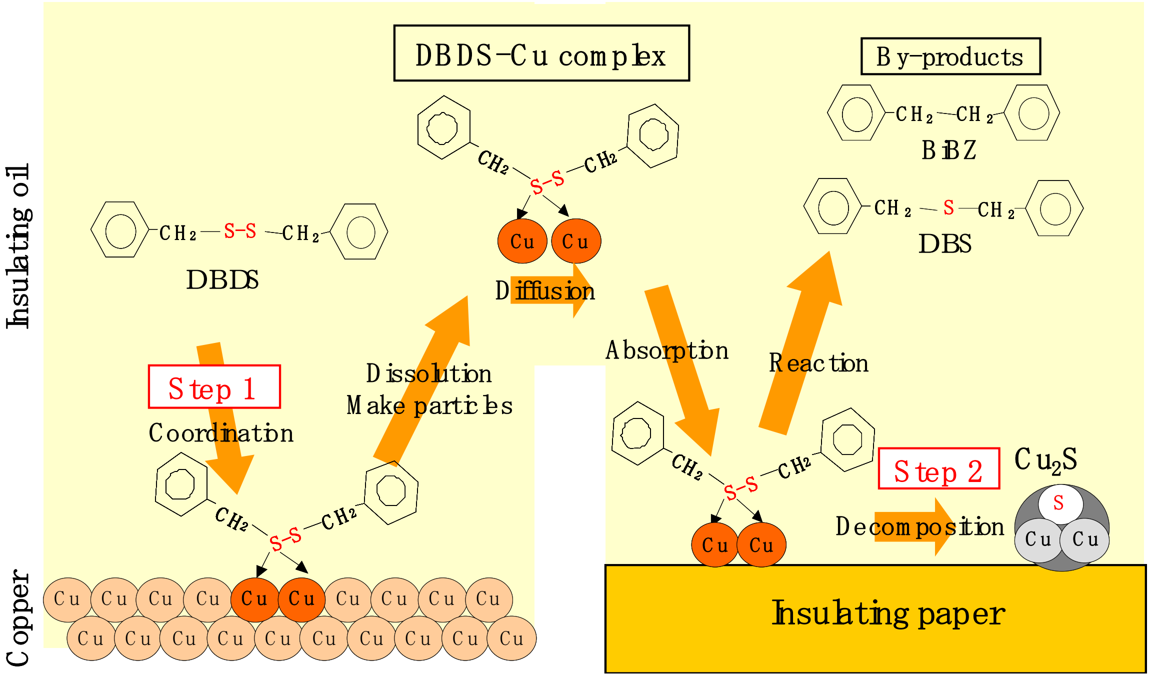

Fig.2 Schematic of copper sulphide formation mechanism on insulating paper using oil-soluble complexes containing copper and DBDS. [8, 9].

The strong influence of oxygen on the transport of copper from the conductor into the paper insulation is not explained by any model presently known. However, at least two potential routes for this effect have been proposed: either (1) by making the paper surface oxidised, and thus a more efficient sorbent for the oil-soluble intermediates [9], or (2) by oxidising some of the existing sulphur compounds in the oil, making them more efficient complexing agents for copper. Extensive oxidation seems to remove sulphur (as well as copper) by the formation of oil insoluble degradation products. There is thus an optimal range of oxygen content for copper sulphide formation on the paper. [10]

Recently, the influence of oxygen on copper sulfide formation has been studied in detail with a new heating test by separating the insulating paper from the copper strip in the insulating oil. The weight of the deposited and dissolved copper was systematically studied under atmospheres of nitrogen and artificial air. The total deposition of copper compounds (mainly sulphide and oxide) on the insulating paper originated from the dissolved copper (copper complex compound) in the insulating oil. The weight of the copper deposited on the insulating paper was increased by the presence of oxygen. Moreover, the influence of the presence of oxygen was investigated individually on insulating oil and insulating paper. The oxidation of both insulating oil and insulating paper was found to accelerate copper migration. [11] Also other studies demonstrate the influence of ageing of oil and paper. [12]

2.1.2 Influential factors

A prerequisite for the formation of copper sulphide is the presence of corrosive or potentially corrosive sulphur species in the oil. In this particular context “corrosive” shall be understood to mean being able to form copper sulphide deposits in (or on) covering paper or pressboard. Such oil need not necessarily be corrosive in conventional metal strip tests such as DIN 51353 or ASTM D 1275, but will be corrosive in IEC 62535. The corrosiveness of some oils may change during service. Furthermore, even though most failures in recent years can be attributed to the presence of corrosive or potentially corrosive components in the new unused oil, the possibility that oil may become contaminated during handling or service must not be neglected as a potential source of corrosive sulphur.

Although the vast majority of problems in recent years have been with naphthenic oils, it cannot be concluded that the problem is restricted to only this type of oil. The ability to form copper sulphide deposits on paper are found amongst both naphthenic and paraffinic oils, and also in oils of an intermediate chemical character. Failures have occurred with both inhibited and uninhibited oils. Even if failures with uninhibited oils predominate, the phenomenon is thus not related simply to the absence or presence of primary antioxidants. [13]

Many oils exhibiting a corrosive behaviour were found to contain significant amounts of dibenzyl-disulphide, and even though DBDS is not the only corrosive sulphur species known in insulating oils, its presence has been related with several failures caused by the formation and deposition of copper sulphide on the conductor and the paper. Its presence is probably related with the majority of cases of corrosivity encountered in the last years. [4, 19]

It was observed in laboratory experiments that copper sulphide deposition on the insulating paper is promoted during oil ageing. Apart from depletion of different metal passivators from the oil and consequently change of oil corrosiveness, this phenomena may be explained by the conversion of sulphur compounds into more reactive forms and the formation of copper complexing oil-soluble compounds. However, it should be noted that the majority of field failures have happened where oil has been relatively unaged, or inhibited, and with a fairly low oxygen concentration in the oil. This apparent contradiction illustrates the difficulty of simulating in lab scale experiments the complexity of real-life processes.

Temperature is obviously a strong influential factor, since most chemical reaction rates are temperature dependant. This is supported by the fact that most failures due to corrosive sulphur have occurred in transformers in countries with high ambient temperatures and/or transformers with high loads. A strong formation of copper sulphide has also been observed in transformers with moderate or severe thermal faults (detected by DGA or after inspection). [14] However, temperature is not the only factor to determine the occurrence, nor the location, of copper sulphide deposits. In laboratory experiments copper sulphide formation was found to occur in the temperature range 80ºC to 150ºC. There are no reports of laboratory tests carried out at lower temperatures.

Oxygen content must be listed here (and is discussed in more detail in sections 2.1.1 and 2.3), since it has a strong influence. However, it must be stated that with our present level of understanding the effects of varying oxygen content are difficult to predict. However, a low oxygen content does seem to be worse than a higher one. Extremely low oxygen contents, though, do not seem to favour transport of copper to the paper. [10] "By "extremely low" in this case we mean less than a few hundred ppm. Even though we would not often expect to see such low levels in the bulk of the oil (not even in sealed transformers) it is very possible that locally, in the insulation, the oxygen content is so low. This may explain why even when substantial amounts of sulphide were formed on the conductor, in some cases there was very limited pentration of sulphide into the papers layers outside of the innermost one. "

The type of paper does not seem to be an important factor. Failures have occurred with thermally up-graded paper as well as with non-upgraded Kraft. In some laboratory tests and experiments the results do not seem to differ between these two types of paper, while in others a difference was observed in tests for corrosive sulphur. Another observation indicating that the type of paper is not important, is that in laboratory tests with corrosive oil, copper sulphide may precipitate also on sulphur-free materials (*e.g.* glass and Nomex).

Paper has also been discussed as a possible source of reactive sulphur. Standard Kraft cellulose contain 300 to 600 ppm of total sulphur. One laboratory study did not show any evidence that a measurable amount of sulphur is extracted from the cellulose to the oil. during 2 weeks at 120˚C . [15] In another study several sulphur compounds, including dimethyldisulphide, were observed as products of paper degradation, with thermally upgraded paper producing higher levels that pressboard. [42]

The influence of electrical fields has so far not been a subject of extensive study. Some observations from dismantled transformers indicate that the field can have a strong influence on where copper sulphide is precipitated. In laboratory experiments the rate of disulphide consumption was affected by a DC field. [16] Non-uniform electrical fields may have an influence on the collection of conductive particles, a phenomenon sometimes referred to as dielectrophoresis. However, to what extent this applies to copper sulphide formation is not clear. It must be pointed out, though, that even if it could be shown that there is a large influence from electrical or magnetic fields, heavy copper sulphide formation have been observed in "no-field" areas of affected windings. Post fault inspection of a HVDC transformer in Norway revealed the highest concentration of copper sulphide in the upper part (turns 190–230) and in the area about 1/3 of the way up from the bottom of the secondary winding. (turns 75 – 95). In general traces of copper sulphide were found throughout the whole winding, also in the bottom turn. The fault was caused by a winding short circuit in turns 87–91. [17]

On load tap changer (OLTC) switching operations involving high stresses (arcing) through the oil have led to extensive copper sulphide formation. This may affect the contact performance. Also, but to a less significant extent, in transformer designs where OLTC and windings are together in the main tank, or in cases where malfunction and oil leakage from the OLTC compartment into the main transformer tank exists, corrosive oil in the OLTC could be a source of copper sulphide contamination in the oil of the main tank.

2.2 Dielectric failure mechanism

There appear to be several different possible failure mechanisms, some of which are listed here:

- In one group of cases, the copper sulphide deposition seems to have started on the innermost paper layer and subsequently affected the following paper layers. Sometimes, but not always, there is also heavy sulphide formation on the conductor. If extensive deposition has taken place, a conductive bridge between two conductors can eventually be formed. In this case failures could happen within designed dielectric stress limits.

  The growth takes place on or within the respective paper layers, and the copper sulphide does not grow in a continuous fashion from one paper layer to the next, nor from the copper surface through the paper layers. It is thus not a single continuous body of copper sulphide. It also noteworthy that it is not necessarily the innermost paper that shows the highest level of sulphide deposition. (See Fig 1d)

Fig. 3. Initial stage of failure. Copper sulphide has grown through all layers of paper, showing as a metallic layer on the surface. There are traces of discharges between conductors. From a disc of a valve winding (neighbouring phase to failed one) in a HVDC transformer.

- Another group of cases is where failures have occurred with moderate amounts of copper sulphide deposition, predominantly on the outside of the paper covering. These cases were with HVDC transformers that were experiencing frequent transients. In one family of cases this was due to frequent line faults, in the other to operation with reactive power compensation (using high “firing angles”). In both cases the repeated transients are believed to have initiated partial discharges in the affected areas, causing cumulative damage to the paper insulation until the point where the PD was no longer quickly extinguished after each transient. When this stage was reached only a short time elapsed before turn-to-turn failures occurred. [18].

- Another interesting aspect is the possible effects of increased conductivity where deposits are formed. Affected areas show significantly increased conductivity. If increased resistive currents generate more heat than can be dissipated locally, this might also lead to failure.[19, 20, 21, 22, 24]

There may well be other failure scenarios than those considered above. Finally, it must be stressed that a transformer is unlikely to fail as soon as there is some precipitation of copper sulphide. On the contrary, some transformer windings contain a lot of copper sulphide and still do not fail. In the end, it is the combined effect of the weakening of the insulation and the dielectric stresses that the winding experiences, that causes the failure.

2.3 Influence of application and design

The majority of failures known so far are within the product groups shunt reactors, HVDC transformers and generator step-up transformers. However, there are also now reports of failures in industrial transformers, small to large power transformers in power grids, and niche applications such as traction line feeders.

Shunt reactors typically operate permanently at their rated load, and are sometimes overloaded, when the voltage exceeds the rated one. Sometimes frequent commutations can cause transients. The negative influence of fast transients is well known and in the absence of effective protection (surge arresters, capacitors, snubbers, etc.) they could act as a promoter for the breakdown, nevertheless a large number of faults were observed in a fleet of shunt reactors operating almost without transients and operating in their rated load range.

HVDC transformers operatiing conditions are also characterised by constantly elevated load, with frequent transients affecting mainly the valve windings. It is remarkable that in most cases only the valve windings failed, but not the significantly more stressed AC windings. Valve windings are typically of the helical type with very low voltage between parallel conductors. There are three risk factors that should be considered; the presence of DC fields, relatively high temperatures and the effect of transients on the valve windings. DC fields may strongly influence copper migration.
Typical of the failed generator transformers was operation with a load close to the rated one. In most, possibly all, cases the failure occurred in the HV winding.

There are so far relatively few reports of failures in open breathing equipment. The optimal oxygen content of oil for the formation of copper sulphide seems to be in a lower range than that typically found in open units. Laboratory experiments indicate that, at least for some oils, the optimal concentration range is from a few hundred to a few thousand ppm of oxygen dissolved in the oil. [10] Many closed transformers have an oxygen content in this range. It must be stressed, though, that many open breathers can work with more or less constant load, in which case they do very little actual “breathing”. In such cases their operating situation resembles that of a closed unit.

Furthermore, it is important to note that high voltage and highly stressed equipment are normally of the closed-type (with rubber bag or nitrogen blanketed); this fact may increase statistically the occurrence of corrosive sulphur related faults in closed transformers.

Enamelled copper winding is a factor which minimises the probability of copper sulphide formation since this leaves very little copper surface exposed for reaction. However, enamelled conductors provide no guarantee that problems will not occur, since there may be joints in the conductors, and other unprotected copper surfaces.

2.4 Influence of service conditions and oil maintenance

As a consequence of the temperature dependence, factors such as load, ambient temperature and cooling settings will all have an influence. Any extraordinary electrical stresses can also increase the risks of failures due to sulphide deposits. In particular the occurrence of large and/or very frequent transients seems to have a large influence. [18]

Oil maintenance actions can also influence the properties of the oil. There are reports that several different reclaiming (or rerefining) techniques can remove the corrosive components in oils, as discussed in section 4.2. There are also cases of oils becoming more corrosive after reclaiming. Investigations are on-going to find out to what extent this is due to conversion of sulphur into more reactive forms, or the effect of the more efficient removal of metal passivators (synthetic or naturally occurring compounds with a passivating action) compared to the removal of the corrosive components in the oil.

3 Diagnostics

There are several different aspects under this heading. One is determining if the oil contains corrosive sulphur, another is if there are already copper sulphide precipitates, and if that is the case, to what extent? This relative ordering of questions is in terms of increasing difficulty to find an answer.

3.1 Oil testing

Due to the ease of sampling oil from transformers, much focus has been on chemical testing of the oils. These can be either qualitative tests, aimed at detecting the presence of corrosive components by the visible effects they have on other materials, or by measuring specific chemical compounds or groups of compounds.

3.1.1 Qualitative tests to detect corrosive components in oil

For many years simple silver strip [DIN 51353] and copper strip tests [ASTM D1275, editions prior to 2005] were used to detect the presence of corrosive sulphur in oils, However, in most of the cases with copper sulphide formation in the insulation in recent years, the oil would pass these tests. “Extended” copper strip tests (*e.g.* ASTM D1275 method B) have been more powerful tools to identify problem oils, but some oils causing problems will pass even such tests. There was a need for a more sensitive and discriminatory test for insulating oils, and such a test involving a paper-covered piece of conductor was developed by TF A2-32.01. The test was proposed to IEC TC10 as a new standard, and was published as IEC 62535 in October 2008. Details of the work to develop this test were given in the A2-32 Interim Report [23]. The use of a machine-wrapped conductor is an essential part of the method.

In some cases it has been observed that in IEC 62535 a strong discolouration of paper, due to severe oil ageing can occur. This may happen with already aged oils, or oils with poor oxidative stability. It has been proposed that in such cases a blank test is carried out with paper only (without copper), in order to distinguish between colour changes due to absorption of oxidation products and those from deposition of copper sulphide.

3.1.2 Oil testing with the purpose of detecting Copper Sulphide formation

To date it seems no or few changes have been seen in the usual oil parameters tested, including DGA, even in samples taken only the day before failures. [24, 25] There appears to be no correlation with copper content in the oil. On the contrary, oils that have caused extensive copper sulphide formation usually have a very low copper content. Nevertheless, in some cases when a high copper content in the oil was found, a significant fraction was found to be present as small copper sulphide particles. Interestingly, this was not the case when any corrosive related problems were reported. [14] Nevertheless, it is still recommended to carry out regular DGA and oil analysis. Some irregularities which can be due to higher temperatures, and which may promote copper sulphide formation can be detected early enough (*e.g.* high CO and CO_2 values), as discussed in section 3.1.4.

As already discussed under section 2.1.1, one possibility being explored is the determination of the by-products from the reaction of DBDS with copper. Dibenzylsulphide (DBS) and bisbenzyl (BiBz) can both be detected by a gas-chromatography method, and their abundance may be indicative of the total amount of copper sulphide that may have been formed from reactions with DBDS. [8] Even though some researchers have supposed that the decomposition reaction of DBDS into copper sulphide (and other by-products) is not strictly stoichiometric, the decrease of DBDS with time in operation has some potential for estimating the progress of copper sulphide formation.

3.1.3 Sulphur speciation

Task Force A2-32.03 on Sulphur Speciation was set up to survey and evaluate, refine or develop if necessary, and recommend suitable methods for the analysis of specific sulphur compounds or classes of compounds in insulating oils.

The analytical methods selected for evaluation included the analysis of insulating oils for :

- Total sulphur content
- Total mercaptans and disulphides
- Dibenzyl disulphide (DBDS)
- Other sulphur compounds: dibenzylsulphide (DBS), octadecylmercaptan (ODM)

This was done by conducting a round robin test (RRT) program with 12 participating laboratories proficient with this type of analysis. The program evaluated both aged and un-aged oil samples in their original state and after spiking with known amounts of the above sulphur compounds. The participating laboratories were asked to analyse each oil sample with analytical instruments at their disposal as follows:

- Inductively coupled plasma (ICP) – total sulphur

- Silver/Silver sulphide (Ag/Ag_2S) electrode titration – total mercaptans and disulphides

- Gas chromatography/electron capture detector (GC/ECD) – DBDS

- Gas chromatography/atomic emission detector (GC/AED) – DBDS, DBS, ODS, other sulphur compounds

- Gas chromatography/mass spectrometry (GC/MS) – DBDS, DBS, other sulphur compounds

- Other methods as available

Not all participating laboratories were able to perform all of the analyses, but the response was sufficient to evaluate most of the methods above.

Results of the RRT program to date indicate the following:

- Analysis for DBDS by GC/ECD is simple, sensitive and relatively reliable. The method can be applied to new and aged oils with little interference and minimal sample preparation to levels below 1 ppm. However, attention should be paid to the possibility of interference from any PCB present.

- Analysis for DBDS can also be accomplished by GC/MS and GC/AED. Analysis by GC/MS is more definitive and can identify other target compounds (DMS etc.) concurrently, but is less sensitive and not as readily available. Analysis by GC/AED has the advantage of detecting all sulphur compounds but is prone to more interference and is a more expensive and less common laboratory instrument.

- Analysis for total mercaptans and disulphides was successfully achieved by Ag/Ag_2S electrode titration. The method is more tedious and requires frequent electrode cleaning, and adjustments need to be made for higher concentrations.

- Determination of total sulphur by ICP gave poor reproducibility among laboratories. Other methods were suggested as substitutes but it was felt that since total sulphur content has little or no proven correlation to corrosive sulphur, it is not worthwhile pursuing further. [26]

Complete details of the RRT will be given in the final report of TF A2-32.03. Some of the methods discussed are also included in the work of IEC TC10 WG 37.

3.1.4 DGA

DGA (dissolved gas analysis) has not been found to be effective as a preventive tool to intercept failures due to copper sulphide formation [24, 25], and seems to be of limited use for the direct detection of copper sulphide formation. Nevertheless it is still useful in the assessment of risk associated with copper sulphide. High load and temperatures, followed by a sharp decrease in oxygen content detected with DGA, should be taken as a condition of high probability of copper sulphide deposition. The presence of overheating and thermal faults in transformers detected by DGA, especially in cases of thermal degradation of solid insulation, elevated concentrations of carbon monoxide and carbon dioxide, followed by intensive oxidation, *i.e.* high consumption of oxygen, is observed to be a condition of concern, according to reported failure cases. A relevant and continuous formation of ethane and methane was detected in equipment where an internal post-failure inspection revealed a strong presence of copper sulphide.

3.2 Tests other than oil tests to detect deposits

At the present time few possibilities have emerged to monitor the growth of copper sulphide, apart from the possiblity to monitor the appearance of sulphide formation by-products in the oil. There are observations supporting the use of dielectric spectroscopy techniques and tip-up power factor tests on windings to give indications of copper sulphide deposits. [25, 27] However, due to the significantly greater capacitance of the winding turn insulation in comparison with the capacitance of major insulation, traditional measurement of dielectric characteristics (tan δ, polarization spectra) applying a voltage between windings or between winding and earthed components may only give indication of copper sulphide contamination when depositions are located in this area. Any deposition residing between winding turns inside the winding will not be detectable. In principle, the capacitive component of excitation current and FRA (Frequency Response Analsysis) test could also serve as a diagnostic tool, with some effect be expected *e.g.* on interleaving windings, whose longitudinal capacitance may constitute several nF, but not on helical type windings.

3.3 Inspection

Moderate amounts of copper sulphide deposition in a transformer may not easily be observed. Proper degreasing of the paper can be needed to observe the deposits unless they are extensive. Transformer windings after vapour phase treatment were successfully and easily inspected in many cases during the factory inspection. With improper degreasing, copper sulphide precipitates could be confused with sludge deposits. Another circumstance making observation difficult is the uneven distribution of deposits. They can be strongly localised.

It should again be emphasized that moderate (or even extensive) amounts of copper sulphide formation may not necessarily lead to failure. In fact, inspection of failed units show that in some areas there may be quite heavy sulphide contamination without any indications of faults. The deposition often follows the existing thermal profile inside the equipment, and is typically located near the top of the winding. However, this pattern is not universal, and all inspections should be carried out in an unbiased and thorough manner.

It must be pointed out that the discolouration can be completely different between naked copper surfaces (contacts, cables, connections, *etc.*) and paper wrapped copper surfaces (conductors). In some transformers with heavily contaminated windings, the naked copper was sometimes found appearing almost brand new. Alernatively some transformers with very dark naked copper surfaces were discovered with very little winding corrosion. In other cases only the inner coils close to the core, that became visible only after a complete dismantling, presented a remarkable picture of corrosion. Therefore inspections should be accurate and as detailed as possible and the final conclusions should be made only then.

4 Mitigation techniques

If the oil has been identified as corrosive, a risk assessment should be carried out. It should include consideration of service conditions, design, age, system importance and manufacturer experience. This is discussed in more detail in section 5. If the result of this assessment is that the equipment is regarded as at risk, several mitigation techniques can be applied. The most widely used so far is the addition of metal passivator. Both oil exchange and on-site oil treatment to remove corrosive components have also been applied. It is sometimes also possible to modify operating conditions in order to lower temperature and dielectric stresses. All of these approaches will be discussed below.

4.1 Metal passivators

The addition of metal passivator is today the mitigation technique that has been used to the largest extent. Passivators used include tolutriazole derivatives such as Irgamet 39 (supplied by Ciba Specialty Chemicals PLC), a mixture of isomers of N,N-bis(2-ethylhexyl)-4-methyl-1H-benzotriazole-1-methylamine and N,N-bis(2-ethylhexyl)-5-methyl-1H-benzotriazole-1-methylamine, and 1,2,3-benzotriazole (BTA) [28]. Several tens to 100 ppm of these substances are typically added to inhibit the reaction of copper with corrosive sulphur.

Metal passivators, have a long history of use in mineral oil, mainly in lubricating oils but also, to a more limited extent, in insulating oils. They have been used not only to counter-act corrosion, but also to improve oxidation stability and to suppress streaming electrification. In particular benzotriazole ("BTA") has been widely used, and also tolutriazole derivatives such as Irgamet 39 have been used in some oils, even before its use was prompted by the copper sulphide problem. In Japan, BTA-additivated oils have been used since the 1970's with no problems due to copper sulphide having been reported. Typically 10 to 30 ppm is added, according to equipment manufacturers recommendations.

4.1.1 Experiences

During the last 4 years probably thousands of transformers have had their oil passivated. Even if it is still too early to make any conclusions about long-term performance, a fair amount of experience has now been collected from the field. It seems that the rate of failures due to copper sulphide has decreased in the last few years. It is generally believed that the use of metal passivators has made a signficant contribution to this. However, the addition of metal passivators is not a guarantee against failures. For instance, in Brazil, more than 200 shunt reactor oils in service were passivated (in most cases between ½ and 2 years after going into service). It has been reported that 9 of theses units failed at between one and 24 months after passivation. One explanation for these failures which led to very corrosive oils and high thermal loads, is that deposition took place very quickly (in the first months of start up), following which passivation was ineffective. This was probably because when the oil was passivated, the paper on the windings was already strongly contaminated by copper sulphide deposits and thus was unable to withstand the electrical conditions that gave rise to the failure.

It has also been proposed that the passivator is less efficient when copper sulphide formation has already started. This may depend on the capability of the tolutriazole molecule to bond to the copper surface, which could be less efficient as more of the copper surface is covered by the sulphide layer
Some experiments carried out under the conditions of the IEC 62535 test seem to support this, while other studies, under less severe conditions, indicate that also copper with a sulphide surface is passivated. [16, 29]

Laboratory experiments show that decrease of the metal passivator content in the oil is followed by an increase of metal passivator content in the paper over time at the test temperature. Migration of metal passivator from the oil to the paper may explain why depletion of significant levels of metal passivator from the oil occur[12, 29] Absorbed passivator in the paper seems to provide protection for some time, acting as a reservoir in protecting the copper surfaces. [30] The possibility that the passivator also directly interferes with the copper sulphide growth on the paper must also not be disregarded. If the passivator is absorbed on the paper then it could also block the nuclei of copper sulphide growth.

Alternatively as observed, a significant depletion of metal passivator, especially in aged oils may be explained by its degradation under the influence of hydro-peroxides decomposition products, which are produced at higher rates in aged oils. Oil oxidation stability is an important parameter that can influence the metal passivators long term stability and performance. [29, 30]

TF A2-32.02 undertook a study on the long-term performance of passivated units. A questionnaire was circulated, resulting in the collection of a limited but significant experience on passivator behavior, from 7 companies Worldwide (4 utilities and 3 laboratories). 72 passivated units were regularly monitored in terms of their oils Irgamet 39 content, in order to verify its stability and efficacy; GSU, Network transmission, Large distribution and Small distribution transformers were included. The duration of the survey which varied from unit to unit, was between 5 to 24 months. Most of the units were passivated with an initial amount of 100 mg/kg of Irgamet 39, but in some cases higher concentrations were used, up to 1000 mg/kg. Some significant decreases in passivator content were observed after the passivation of the oil. Within the observed population, 66% of units showed a stable concentration in time, 33% indicated a depletion. During the study none of the surveyed equipment failed or was inspected for other reasons, so no further information is available from this experience. Cases where a depletion was observed may be divided into two families:

- a moderate decrease is observed in a few months after passivation, leading to a final steady concentration (approx 60-70% of the added amount)

- a regular and progressive depletion which reduces the passivator concentration to a very low level.

The former case may probably be attributed to an initial equilibration of the passivator distribution between the oil and the polar materials (paper, wood, metal surfaces); this is not a non-efficient passivation, but a normal distribution of the passivator in the materials which need to be protected against corrosion. An example is in the following figure.

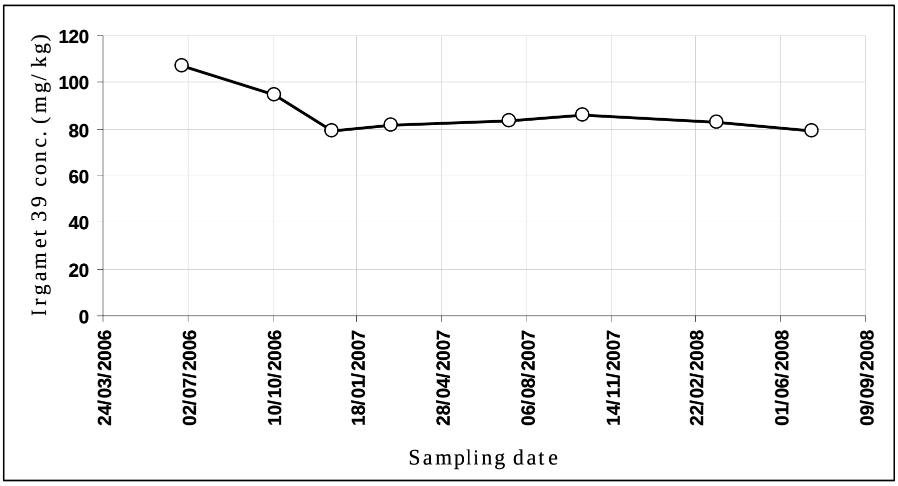

Fig.4 - Initial depletion of passivator in a distribution unit, followed by a steady concentration

The latter situation (continuous decrease of passivator) has been observed in a number of cases, and still does not have a clear explanation. An example is in the following figure.

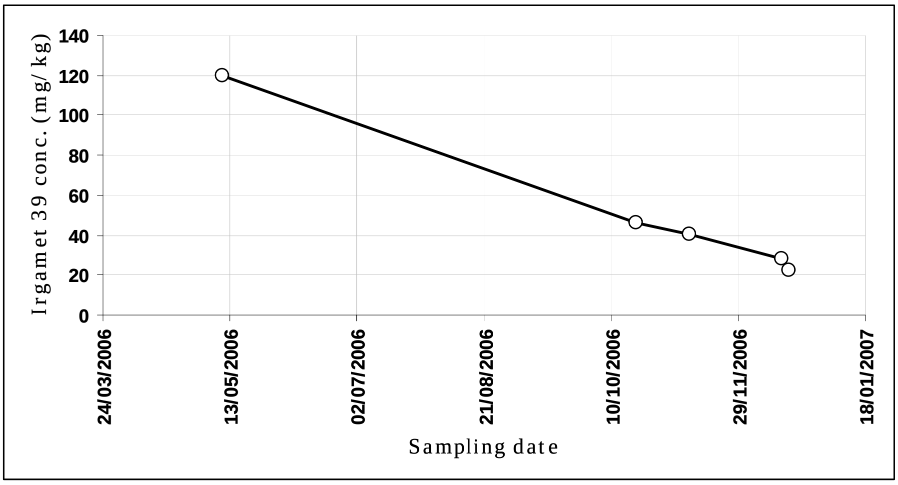

Fig.5 - Example of progressive depletion of passivator in a GSU unit

Laboratory experiments confirmed that the passivator may deplete in conditions of high thermal stress (e.g. during the conditions of IEC 62535), but the passivator was consumed also in transformers under normal thermal conditions. In some cases this depletion was associated with aged oils (with appreciable acidity and sludge formation), but this was not always the case. Equipment submitted to a second passivation when the Irgamet 39 had decreased below an acceptable concentration, usually showed a new depletion after the topping up. An example is given in Fig. 6.

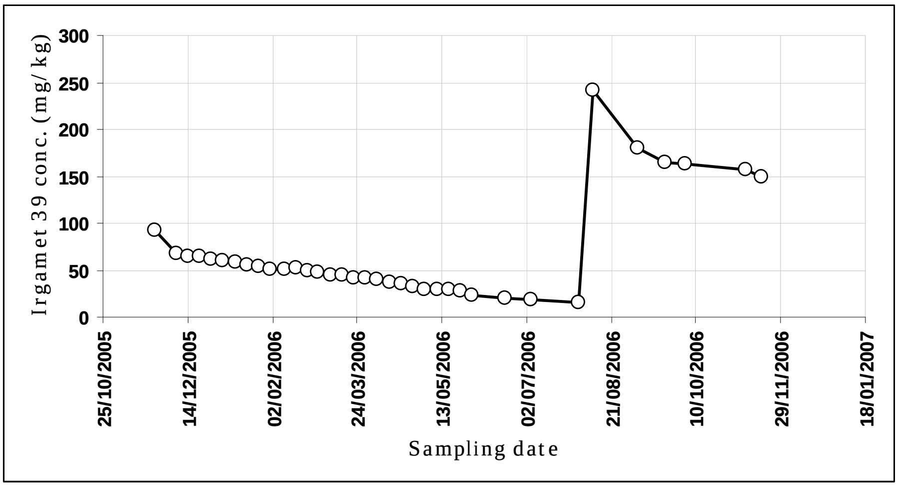

Fig.6 - Example of progressive depletion of passivator in a GSU unit, even after top-up of Irgamet 39

The initial concentration seems to have no influence on the stability of the passivator, units passivated with 100 mg/kg lost the passivator as well as units with 300 mg/kg.

When the passivator content in the oil decreases below a certain level the oil may revert back to its original corrosive state (oils containing 160-180 mg/kg of DBDS were found to become corrosive again when the passivator's content decreased below 20-25 mg/kg). [37] It is not clear if the decay of the passivator actually influences the level of protection of the copper conductors; laboratory experiments have shown that once the copper surface is covered by a protective layer of passivator, the protective action continues to take place even if the concentration of passivator in the oil drops. Although it has also been shown that oils where the passivator depletes severely, revert back to being corrosive. It is not known how much of the added passivator reaches the surface of the conductors, and how much is trapped in the polar materials. As a general remark, this experience demonstrates the importance of monitoring passivated units to control the passivator concentration.

4.1.2 Monitoring of passivator content

Considering the above it essential to monitor the passivator content during service. The content of benzotriazole type metal passivator in oil can be determined by HPLC (high performance liquid chromatography) in combination with a sample work-up using liquid-liquid extraction or solid-phase extraction, in a manner very similar to that used for example in furane analysis.[31]. A method for tolutriazole derivatives (specifically Irgamet 39) has been developed by TF A2-32.02, on the basis of the experience of several laboratories participating in the study. Details are to be included in annex B of the new edition of IEC 60666. The method will be posted on the SC A2 web site until new IEC 60666 is published.

4.1.2.1 SPE-HPLC-UV method - outline

The analysis was carried out after a pre-treatment of the sample by SPE (Solid Phase Extraction) on silica-gel cartridges rinsed with hexane or another suitable solvent, to separate the analytes from the hydrocarbon matrix. The analytes, extracted in a suitable polar mixture of water and methanol, were submitted to separation via RP-HPLC, and finally detected with a UV-Visible detector at a wavelength of 260-270 nm. Using the same analytical conditions BTA (benzotriazole, another triazole derivative widely used in transformer oil) may also be separated and detected, but it was not included in the study of TF 02, having been the subject of study by a previous Cigre working body. [32]

4.1.2.2 SPE-HPLC-UV method - performance

TF A2-32.02 evaluated the applicability of the method to detect concentrations of Irgamet 39 between 5 and 150 ppm approximately, both in unused and aged mineral insulating oils. Two RRT were done, with 9 laboratories participating. The first RRT investigated unused and used oils, and it was found that the method gave accurate and reproducible results in the concentration range 5 to 150 ppm with unused oils, but was less accurate with aged oils. The second RRT was thus dedicated to used oils (acidity 0.03 to 0.4 mg/kg), and showed very clearly that the determination of Irgamet 39 may be influenced by the aged condition of the oil; the figure below depicts the behaviour of accuracy with the acidity of the oil.

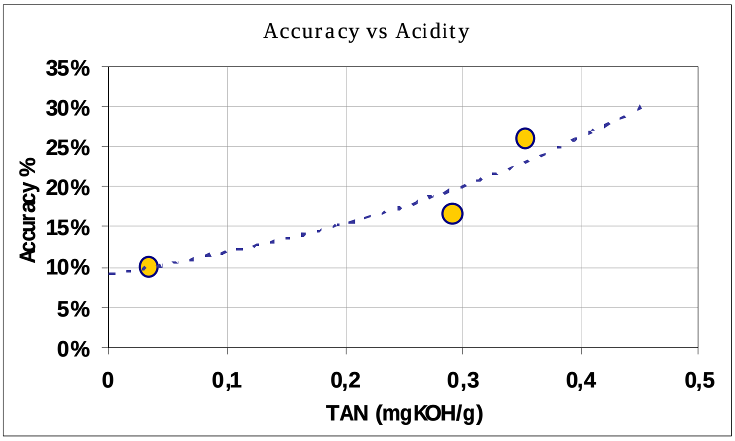

Fig. 7 Influence of the oil acidity on the accuracy of Irgamet 39 determination with SPE-HPLC-UV method.

The reasons for this interference from the aged oil are not completely understood. One possibility is that a high content of acids and polar substances may interfere with the active absorptive sites during the SPE; this problem may be reduced by properly setting the extraction conditions (see method for details).

The two RRT allowed some guide values for the precision data to be established, which are described in the following table (r = repeatability, R = reproducibility).

Irgamet39 Concentration	*Unused oils*	*Middly aged oils (acidity < 0,2)*	*Heavily aged oils (acidity > 0,2)*
<50 mg/kg	r ≈ 10% R ≈ 15%	Not evaluated	Not evaluated
>50 mg/kg	r ≈ 5% R ≈ 8%	r ≈ 15% R ≈ 20%	r ≈ 15% R ≈ 40%

4.1.3 Side effects (“stray gassing” etc.)

There are a significant number of reports of increased hydrogen and carbon dioxide formation when the passivator is added to oil already in service. Similar effects have been observed also in accelerated laboratory experiments. If the rate of hydrogen formation is strongly affected by the addition of metal passivator, this may affect the interpretation of DGA data for such units. It has been suggested that hydrogen evolution observed in units in service is likely to originate from other sources (overheating) rather than as a direct consequence of metal passivators addition.[33] However, that the phenomenon so far was was not reported with originally passivated oils, indicates that the status of the oil also has some influence. Experience with the use of BTA-additivated oils in Japan since the 1970s, show no examples of an increase in hydrogen gas or carbon oxides that have been reported.

4.1.4 Other passivators

The application of mixtures of inhibitors and metal deactivators is well known and has been used in the lubricant industry for the improvement of oil performance. Blends of different types of inhibitors are available, and have been used in transformer oils. They can consist of phenol or amine type inhibitors and metal passivators of varying composition. One company has presented a blend under the label “sulfur inhibitor”, that is a liquid concentrate of blended metal passivators BTA/TTA derivatives, phenol or amine based oxidation inhibitors and “sulphur stabilizers”, *i.e.* components inhibiting the reactions of sulphur compounds. These mixtures may have better long term stability and performance over conventional metal passivators and inhibitors alone, due to the potential synergism of phenol/amine based inhibitors and metal deactivators in suppressing the formation of oil oxidation products and intermediates in copper sulphide reaction. The role of phenol/amine based inhibitors acting as radical scavengers is to prevent the generation of oxidations products in the oil such as hydro peroxides, which should give a lower rate of metal passivator consumption by this route.

4.1.5 On-site passivation

Metal passivator is usually added as a stock solution, dissolved in insulating oil. Such stock solution is commercially available, but some service providers prepare the stock solution on-site, with oil from the actual unit. The stock solution can be added via a degasser filter (taking care not too exceed limits outlined in section 4.1.6), but it can also be injected in the cooling loop.

4.1.6 Treatment of passivated oil

To date, there is little experience reported of passivator behaviour during oil maintenance treatments, *e. g.* reclaiming and reconditioning. The first experiences from the field show that reclaiming results in heavy loss of passivator, due to its strongly polar nature. There are conflicting reports on the degree of loss of passivator during degassing or reconditioning. However, reconditioning on-site at 60^{O}C and 1mBar has been performed with no significant loss of passivator. Laboratory scale vacuum filtration under the same conditions yielded similar results, with a decrease of the passivator content by 3%. Another full-scale test, where 14 m^3 of passivated oil in a reactor was circulated through a thermo-vacuum plant at $12m^3$/hour, at

70-80ºC and 0.3 torr for 6 hours resulted in the loss of only 1% of the initial passivator content. In both these cases the passivator used was Irgamet 39. However, should a passivated oil need to be treated, and it has not already been established that the treatment in question has no significant effect on the passivator, it is essential after the treatment to analyse the passivator content and to re-passivate to the original concentration if necessary, or at least to test the oil for corrosivity.

4.2 Removal of corrosive sulphur from oil in service

Available oil treatment techniques may be divided into two groups, techniques based on the removal of corrosive sulphur compounds, and others based on the conversion of sulphur compounds. Combinations of these techniques are also available. Different treatments with activated earths may include removal of the corrosive sulphur compounds by absorption, and/or conversion into non-reactive compounds (chemisorpton). The Liquid/liquid extraction process is based on the selective extraction of corrosive sulphur compounds using solvents.

Several techniques have been proposed, and in some cases are already being used for the removal of corrosive sulphur from oil. These include the use of :

- continuous on-line treatment with sorbents [34, 35, 36]

- “selective depolarisation” (a combination of reagents and sorbents) [37]

- mobile on-line reclaiming, with reactivating sorbents [38, 39]

- treatment with KOH/PEG, similar to established PCB removal technology [40]

- liquid-liquid extraction [41]

Continuous on-line treatment, selective depolarisation and mobile on-line reclaiming have been applied for the treatment of oils in service. Treatment with KOH/PEG was tested off-line on pilot transformers. Liquid-liquid extraction is in development for field applications.

4.3 Oil exchange

Another successfully used technique for corrosion mitigation is the change of the original oil. In Brazil for instance, the oil of 45 shunt reactors has been changed without any failure after this process. In one population of 21 transformers preventive action was taken in July and August 2005. Because of the shortage of safe oil, only five reactors could be retrofilled and the remaining 16 were passivated. As of December 2006, eight of the latter group had failed in service, respectively at 33, 102, 136, 168, 284, 363, 478 and 590 days after passivation. No failures have so far occurred for any of the retrofilled units in this group.

Some precautions should be considered when oil replacement is carried out:

- a laboratory corrosion test (mixing: 9 parts of new oil and 1 part of corrosive oil) should be performed first

- a small extra quantity of oil will be needed to rinse the interior of the tank and the immersed parts. In order to reduce the residual presence of corrosive oil it is important that the tank, the core and the windings must be cleaned as fully as possible. Experience with the refilling of power transformers filled with oil contaminated by PCBs, demonstrates that residual oil can be kept in the range 5-10 %. Exactly what level of exchange can be achieved depends on the design of the equipment.

- Repeat the corrosion test after 30-90 days, in order to verify the effectiveness of process because a little release of original corrosive oil from paper can be expected.

4.4 Modified operating conditions

Since temperature is an accelerating factor, any measures taken to decrease temperature should decrease the rate of copper sulphide formation. Thus, lower loads and increased cooling could both help in this respect, in cases where the oil has been found to be corrosive. However, both these measures may have limited effect in real life. In some cases, a substantial lowering of oil temperature was achieved by forced cooling. In Brazil has been monitored for some time the thermal performance of shunt reactors which were retrofitted with forced air cooling and found a reduction of some 10°C in the hottest spot temperature as indicated by thermal imaging (see figure 8). [24] The possibility of increased cooling should always be considered. Not only is it clearly an effective way of slowing down sulphide formation, there are also the additional benefits of slower ageing of oil and paper.

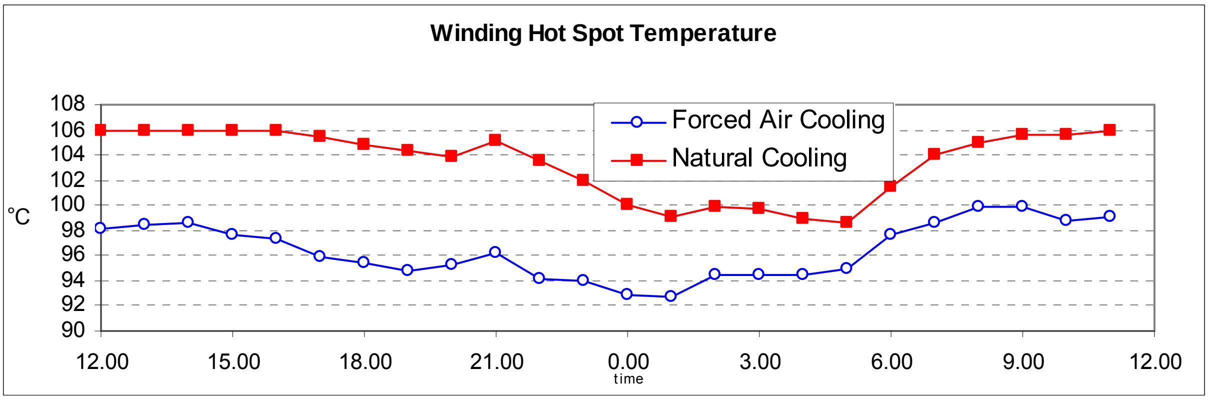

Figure 8. Daily recording of winding temperature in two twin shunt reactors with different air cooling mode

Transients are believed to trigger the break-down of affected insulation, once deposits are formed. If it is possible to reduce the occurrence of transients, this could lower the risks.

4.5 Removal of deposits

It must be stressed that none of the mitigation techniques proposed so far will remove sulphide deposits already formed. They will only retard, or at best stop, the process. So far no methods have been suggested for the removal of copper sulphide from the insulation. This may prove difficult due to the stability and low solubility of copper sulphide, but a solution may be developed in the future.

5 Recommendations

This section by TF A2-32.04 deals with converting the knowledge gatherered so far, and presented in the previous sections, into practical recommendations for users of transformers. It deals one at a time with the different stages where some action might be taken. The first line of defense is to avoid using oil with corrosive sulphur, the second is to try to limit the extent of sulphide formation when the presence of corrosive sulphur is already a fact, and the third is to limit the risk of damage when significant formation of sulphide formation may already have taken place.

5.1 Oil for filling, topping up or exchange

All oils should be tested for corrosiveness according to IEC 62535 before it is added to a transformer. Several oil specifications now also include ASTM D 1275B although experience so far indicates that an oil passing IEC 62535 is very unlikely to fail ASTM D1275B. It is important that contamination by corrosive oil is avoided at all stages of transport and filling. Check for passivator content, and in the case of oil containing passivator, monitor the level by yearly oil samples.

5.2 Supervision and maintenance of oil in use

The following actions are recommended for any utility or owner of power transformers and shunt reactors who is concerned about the effect that copper sulphide has or will have on their transformers and reactors.

For large transformer fleets it is recommended to focus first on the units delivered in the last 20 years and specially the GSUs, shunt reactors, HVDC transformers, industry transformers and highly loaded transmission transformers, and secondly, to focus on all other power transformers.

5.2.1 Screening procedure – data collection

- Identify all units delivered since the end of the eighties, or units having undergone major top-up or oil change (> 20%) between end of the eighties and 2008.

- during the screening, give priority to transformers and reactors matching one or more of following conditions:

  a. High load, high voltage, high temperature
  b. No spare units are available
  c. Sister units had suspect failure in last years
  d. Voltage level ≥ 220kV

- Find the answers to the following questions:

  1. What is the year of manufacturing ?
  2. What oil (product) is used ?
  3. Do the windings have enamelled copper conductors?

4. Free breathing or sealed conservator system?
5. What is the yearly average load in the transformer?
6. What is the yearly average and maximum top oil temperature ?
7. Indication from DGA: typical level and trends in oxygen content, or symptoms of overheating (diffused or localised) ?
8. High electrical stresses (mainly frequent transients, e.g. switching, lightning etc.)
9. OLTC oils mixed with transformer oil ?

- For the prioritised units take oil samples, and analyse the oil to:

  - o Detect corrosive sulphur and potentially corrosive sulphur according to IEC 62535 (section 3.1.1)
  - o In case of negative corrosiveness, check for the presence of passivators (section 4.1.2)
  - o Detect DBDS content in the oil in case of positive corrosiveness, or in case of negative corrosiveness due to the presence of passivators. (section 3.1.3)

5.2.2 Screening procedure – decision making

- Use the flow chart in figure 5 on page 29 to identify suitable actions and the probability of copper sulphide deposition which could lead to a failure. *N.B.* “probability” here is related to the risk that significant Cu_2S formation is going on. The scheme does not deal with the situation when the insulation is already seriously affected by sulphide deposits.

Some notes on the flowchart:

1. After any action is taken, refer back to the flowchart to verify the new condition into which the unit falls.

2. Due to the lower expected efficiency of passivation in case of conditions leading to a “high probability of copper sulphide deposition”, passivation should be seen mainly as a preventive action to delay further corrective action, that is able to remove the source of corrosiveness. Especially when the oil shows sign of ageing, a more frequent monitoring of the passivator content is recommended, until its rate of decay is established

3. The flowchart is an attempt to deal with a complicated situation in a simplified way. It is a compromise; too much simplification would make it into a tool too coarse to be of any real help, while attempts to bring in a lot of detail would make it unmanageable. It represents the working groups best knowledge at the time. Further research may lead to its re-evaluation and refinement.

5.3 Actions for old oil in units, more than 20 years in service.

For units being in service for more than 20 years it is not easy to give good recommendations of actions. The expected residual lifetime could vary significantly and the probability of a failure due to copper sulphide will be between very low and very high. A risk assessment, for each unit, considering not only oil but system importance, design, operating condition, maintenance cost, general technical condition as well as manufacturer experience is necessary before any decisions of actions are taken. Any actions chosen should be in view of the risk level and the cost involved.

Section 4.2 (Removal of corrosive sulphur from oil in service), and section 4.3 (Oil exchange), describes some actions on oil to prevent further copper sulphide deposit in the windings, which could be applied if the oil is tested as corrosive, and the risk assessment makes it worthwhile. Passivation of aged oil may be ineffective, due to the already high concentration of degradation products in the oil. These processes must be further studied.

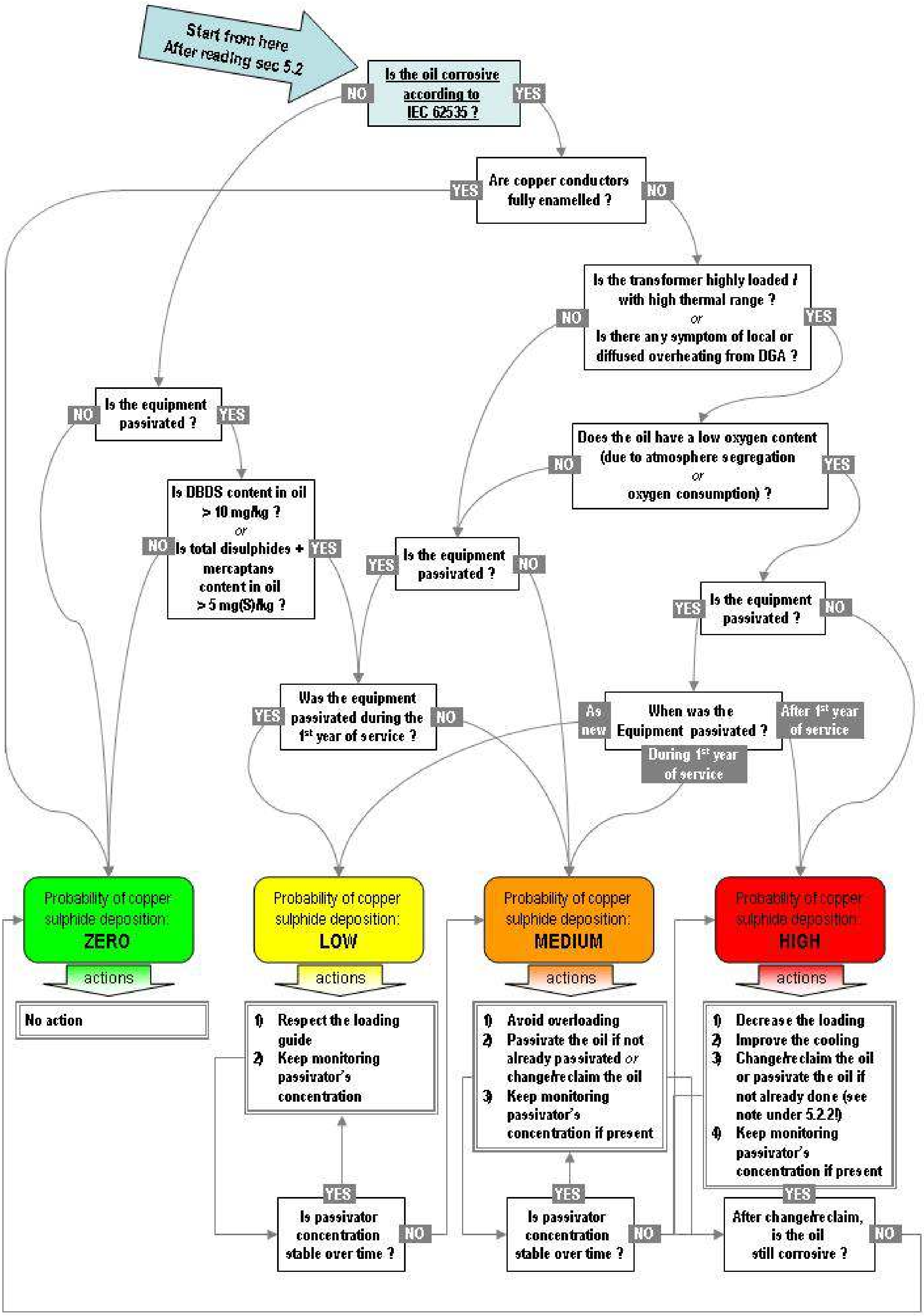

Fig 9. Flow chart for decision making associated with corrosive oil and risk of on-going Cu_2S formation

These actions will not have any effect on the copper sulphide already in the windings but it will minimise further copper sulphide formation, and the probability of a failure due to copper sulphide could be considered low or medium.

5.4 Actions for units with significant Cu_2S contamination

The above recommendations deal mainly with ways of stopping the sulphide formation process. However, no matter how successfully this process is suppressed, there may in some cases already be substantial amounts of copper sulphide formed. As mentioned in section 4.5 no way of removing these deposits are known to date. So what can be done in such cases to decrease the probability and limit the consequences of failures?

- Ensure measures are taken to limit further sulphide formation, according to section 5.3
- Avoid or limit, if possible, overvoltages and transients
- Rewind the unit or replace
- Have spare units available

Oil refurbishment and rewinding should always be compared in cost and effectiveness in comparison to a new equipment acquisition.

6 Concluding remarks – future work

The members of this WG are the first to admit there is still a lot to learn about this phenomenon. We see two main areas of activity for new working bodies dealing with copper sulphide. For each of these we can list a number of aspects or questions.

6.1 More precise risk asessment.

More precise risk assessment in general will certainly be demanded. IEC 62535 seems to be an adequate tool to screen out new oils that might cause problems. It might be too severe a test for aged oils, though, considering the large fraction of such oils that are identified as corrosive by this test. As more is learnt about the mechanism and the influential factors, it should be possible to more accurately find the appropriate level of action for different cases of aged oil testing as corrosive. Some aspects which deserve more studies include:

- The influence from other sources of reactive sulphur than the oil itself.
A lot of focus has been on oil containing significant amounts of corrosive, or potentially corrosive, sulphur when new. From what is known today, this focus was justified, but it may have been at the expense of studies on the effects of sources of contamination, or of processes leading to formation of harmful sulphur species from those (believed to be) harmless.

- The influence of electrical and magnetic fields.
Very few studies are reported, but there are indications this could influence the extent as well as the location of copper sulphide formation.

- A better understanding of the influence of oxygen, and other details of the copper sulphide formation mechanism.

- More statistics to be collected, including DGA history of failed units.

6.2 The study of long-term effects of mitigation techniques

In the area of mitigation techniques, substantial progress has been seen. A knowledge of the applicability and limitations of metal passivators and oil exchange has been developed, and also ways of removing the corrosive components of oil in service. Nevertheless, more studies on the efficiency and long-term effects of mitigation techniques are desirable. Prioritised areas here are:

- The significance of stray gassing after the addition of passivator, and the possible relationship with rapid passivator consumption.

- Further studies of effects of passivator when significant amounts of copper sulphide are already present, including the possibility that at certain temperatures the transport of metal passivator from the oil to the windings can be overtaken by faster reaction of copper sulphide formation and deposition

- The function of paper as a reservoir or depot of passivator, and to what degree passivation of the paper is an important part of the function of the passivator.

- A better prediction of passivator stability, from more complete mapping of influential factors

- Follow-up of passivated and reclaimed units, including the influence of operating conditions.

- New methods for the removal of corrosive sulphur from oil, and of copper sulphide from the insulation.

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