Failures due to copper sulphide in transformer insulation

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In recent years a number of failures of transformers and reactors have occurred due to copper sulphide formation in the windings.

The failures affected different classes of equipment [1, 2, 3, 4, 5, 6]. They involved mostly equipment operating at elevated average temperature, although (with some exceptions) within accepted temperature limits, and were normally without warning from commonly used oil tests, including DGA. Several different oils were involved. All oils fulfilled present IEC and ASTM specifications when new but, at least in some cases, the oils changed during operation, turning corrosive and causing growth of Cu_2S. Today there are no reliable and universally known and accepted methods to identify units at risk or oils that may cause problems, nor diagnostic techniques to identify already affected equipment. There is so far quite a low level of general understanding of the phenomena which include the influence of transformer materials, temporal development, temperature dependence, service conditions, impact of design, etc.. Some mitigation techniques, namely the addition of metal passivators, have been tried with apparent success, but more knowledge of possible side effects and long term stability of these is needed.

Copper sulphide formation

There seem to be several different manifestations of the copper - sulphur interaction. Sometimes increased corrosivity is seen in the traditional meaning of the word, i.e. with blackening of copper and silver surfaces. This may be a serious problem in some cases. However, the larger problem seems to be the precipitation of semiconductive copper sulphide in or on the solid insulation, something which cuses significant deterioration to its dielectric properties. In some cases growth of copper sulphide is found starting at the innermost layer of covering paper on the conductors, eventually growing through several layers. In other cases copper sulphide is found deposited on the outside of the conductors' paper wrapping, or on spacers. Examples are shown in Figs. 1 - 3.

The details of the chemical reactions leading to these phenomena are not yet well known. Some active sulphur containing compounds are obviously needed. There are several possible sources of such compounds, including contamination from unsuitable materials and handling of the oil, but it is already clear that some oils contain significant amounts of potentially reactive sulphur. Generally sulphur compounds have been considered important for the oxidation stability of oils. There are indications that it is, at least partly, the same bivalent sulphur compounds that act as peroxide scavengers (and in that role suppress the oxidation of oil) that may also have corrosive effects. They may possibly, under some conditions, be corrosive in themselves, but there is the more likely possibility that more aggressive sulphur organics, such as mercaptans, are formed during operation.

Accessibility of copper is also an important factor. Conductors without enamel are clearly more vulnerable to growth of copper sulphide from the inside, but even with enameled conductors copper may be available elsewhere to be dissolved, transported and eventually precipitated as sulphide. All chemical reactions proceed at a higher rate when the temperature increases, and there certainly appears to be some correlation with temperature, but sulphide formation is not always observed in the areas with highest temperature, nor are there usually any signs of very high temperature (such as low DP values of paper) where the sulphide has been formed. A low oxygen content of oil seems to promote sulphide formation. Such conditions are found primarily in sealed units, and unsealed units with uninhibited oil, especially working at high and constant load.

Fig. 1: Example of copper sulphide growing through several layers of covering paper.

Which units are at risk

The most important task for both utilities and manufacturers is to identify the units at risk. This means evaluation of those factors which will lead with a high probability to a failure unless counter-measures are taken. According to present knowledge these influential factors include a combination of:

- *Oil:* an oil with clearly corrosive properties according to the tests applied (e. g. prolonged ASTM test with a copper strip, prolonged ASTM test with a copper strip wrapped with kraft paper, paper deposition tests), or an oil which is already known to have caused problems related to copper - sulphur interaction.
- *Temperature:* an application where the unit is operating at elevated average temperature, although within accepted temperature limits. Such applications are mainly highly loaded GSU, rectifier, HVDC transformers or shunt reactors.

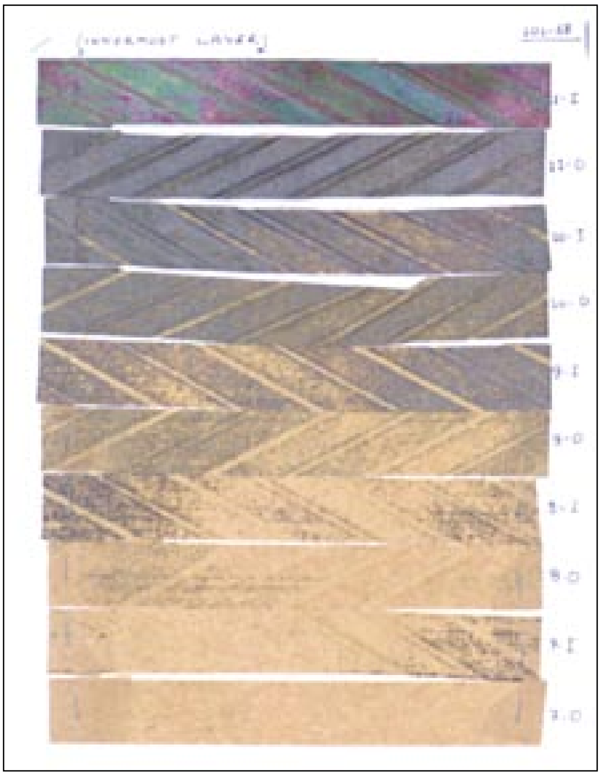

Fig. 2: Different layers (both sides shown) of covering paper from a conductor with varying degree of copper sulphide deposition.

- *Design:* a design which allows only restricted access to oxygen, e.g. rubber bag or nitrogen blanketed, with a winding of unvarnished flat wire.

Since gas in oil behaviour, even shortly prior to failure, does not give any sign of an eventual deficiency, the traditional laboratory diagnostics is not able to detect early stages of copper sulphide formation [7, 8]. Further work will be needed for an evaluation of oil analysis parameters, which may give some indication of an ongoing process.

In the long term, the possibilities to use non-intrusive methods (dielectric spectroscopy, PD measurements, etc) for the detection of sulphide formation should also be explored. Direct inspection of the active part in units at potential risk is unpractical and not recommended. Every utility has so called "never clarified" failure cases in its statistics. Due to the diversity of copper sulphide appearance it is highly probable that some cases in the past were not properly identified. Deposits on paper, perhaps mixed up with sludge, and/or blackening on copper have often been considered to be a consequence of high temperatures causing breakdown products. Deposits of copper sulphide are to be seen clearly often only after degreasing and careful de-winding of the separate paper layers down to the copper conductor.

Fig.3: Example of copper sulphide deposited on spacer and under spacer. Similar deposits may also sometimes be seen on the outside of conductors in the area between the spacers.

The strict recording of failure cases, with all available data, photos and samples will be inevitable in future in order to reveal certain problems and help finding the root causes of the failures.

How to avoid the problem in new transformers

According to our present knowledge the most decisive factor for Cu_2S formation is the oil composition. Therefore, our first priority is to select a non-corrosive oil.

Today's oil specifications are not sufficient to identify oils that may cause this problem. All the oils that have caused failures due to copper sulphide formation test as non-corrosive when new, with the copper strip or silver strip tests used in current ASTM and IEC specifications (ASTM D1275 and DIN 51353 respectively). Most national and company specifications use the same tests, even though some have recently introduced more severe tests.[9] There is an urgent need to find and introduce tests to identify oils that can become corrosive and cause copper sulphide formation.

The possibility of using metal passivators to mitigate the problem has already received much attention. Laboratory test results so far for new oils have given encouraging results. Although no adverse side effects of using passivators to new oils have been seen so far, or are anticipated, further studies to ensure a safe long-term effect are needed.

How to minimize problems with existing transformers

Short term considerations - metal passivator.

A technical solution based on laboratory tests has been proposed. This involves adding a passivating agent to the oil. The passivator is a "tolutriazol" derivative, very similar to BTA (benzotriazol), however easily soluble in oil, and provided as a concentrate to be diluted in oil, thus obtaining a final concentration of 100 ppm. This is made in order to prevent (in new oils) or interrupt (in used oils) the sulphide formation process. The passivator adheres to the copper, and blocks the reaction of other molecules with the conductor surface. The passivator is expected to last the whole equipment life time (without requiring to be topped up), not to have any adverse effects on paper, copper or other materials used, and to not affect the analysis results for oil.

As a limiting factor there is the fact that it only suspends the process; the process will not be reversed in already affected equipment. Field experience of passivator used to suppress copper sulphide formation is of course so far very limited. Many transformers and reactors in different parts of the world have had the oil passivated in the last few months. It is too early, though, to make a proper evaluation of the effect so far. However, there is positive experience with long-term utilization of benzotriazol for mitigation of static electrification effects.

Long-term considerations

The diversity of the copper sulphide problem suggests a variety of mechanisms (chemical, physicochemical) which contribute to the formation of deposits, mainly influenced by oil composition but to some extent also by service conditions and design. A better general understanding of the ongoing processes is required in order to develop, not only a pragmatic, but also a technically mature solution.

What is sure is that this problem will change the oil specification philosophy of many utilities and manufacturers. It is important to emphasize that the corrosive sulphur problem faced today is different from that identified in the past. The "old" one resulted from deficiencies in oil refining, and thus was present in the corrosive form even before contacting electrical equipment. Today, the corrosive compounds seem not to be present in the oil before contact with copper. They are more likely formed from the conversion of such sulphur- organics that at first have mainly beneficial characteristics as oxidation inhibitors. However, as a result of operating conditions, such as high temperatures and low oxygen contents, they are transformed into more aggressive compounds.

Test methods need to better evaluate the influence of sulphur compounds in the oil formulation. We have different situations, since oils may affect copper and paper to very different degrees. The new tests must be able to identify the different situations in order not to unfairly penalize future formulations that may provide good performance, especially in terms of oxidation stability, simply because they contain some sulphur compounds. Furthermore, a change in the sulphur requirements for oil will surely lead to a number of changes in other properties.

A balance must be maintained between different requirements. In the future, we will be required to breach some paradigms, such as thinking that an insulating oil requiring artificial additives must be a "bad base" oil. From now on, we expect more use of well refined inhibited insulating oils, i.e. oils with very low sulphur content, and where the stability requirements - specified in the various standards - have been achieved by adding a synthetic anti-oxidant and possibly also a metal passivator. We may also see a shift from a "general" to an "application and design" dependent oil specification, for reliable transformer service. Oil and transformer manufacturers, users and consultants will meet the challenge of a new transformer oil specification in the near future.

Conclusion

It is necessary to work intensively in several directions. Several urgent aspects have been identified, each with more or less priority. These aspects are: a) Oil testing and specification issues, b) Methods to identify units in danger, c) Recommendations for counter-measures to stop or retard the processes, d) Improved understanding of this complex problem. All these need to be addressed, but some amendments to standards and specifications cannot wait until a complete understanding of the involved phenomena has been achieved.

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