Corrosive sulfur in transformer oil

Technical bulletin on problems, consequences and recommendations for treatment

Power Transmission and Distribution

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In the last years there has been noticed an increase of cases where relatively young transformers failed after several years of service. The cause of those failures is a dielectrical breakdown of the turn to turn insulation: conductive layers of copper sulfide, growing from inside to outside through several paper layers or the formation of similar conductive surfaces on the outside of insulating parts cause a flashover.
This phenomenon creates a lot of uncertainties to manufacturers, users and independent consultants. A lot of questions arise, among others: have transformer oils reached their physical limits? Which units are at risk? What ways to go in the future?

Even if there has been detected only a small number of those problems worldwide, the Siemens Transformer Group wants to make sure that all their customers are aware of possible risks, to enable them to take the necessary measures at the right time.
With this flyer Siemens likes to present a concept, characterizing this phenomenon and recording current investigation results concerning the formation of corrosive sulfur as well as possible mitigation techniques.

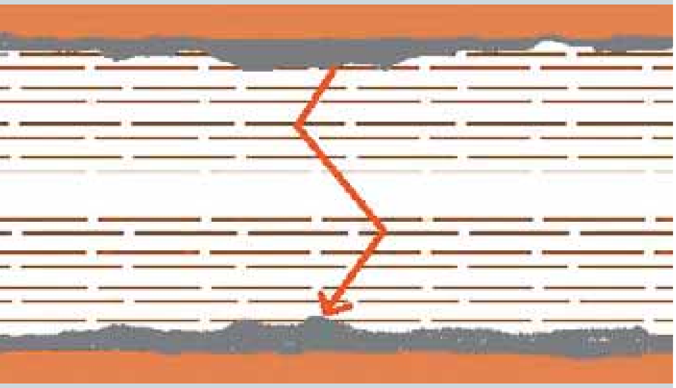

Fig. 1: Paper insulated conductors with a growing deposit of conductive copper sulfide from the inside to the outside layers

Fig. 2: Dewrapping of a paper insulated conductor showing deposits of copper sulfide on the paper insulation

Affected Equipment

The largest number of affected units world-wide is reported within the group of reactors, HVDC transformers and step up transformers, working near to rated load or overload and/or at high ambient temperatures. The transformers known to have failed due to corrosive sulfur are mainly part of closed type units (rubber bag) and are manufactured with paper insulated flat wire. The insulating oils had mainly been non- or partially inhibited oils with a low refining grade.

What is happening?

High voltage windings in GSUs and reactors are manufactured as interleaved windings for an appropriate impulse strength very often. The conductors are paper-insulated, considering the necessary safety margin. In case of conductive deposits of copper sulfide the safety margin is reduced and at a certain point a breakdown will occur. Furthermore the deposits of copper sulfide increase significantly the conductivity of the insulating parts (Fig. 1). In this case small gas bubbles can be produced which will also locally diminish the electrical strength significantly. External factors like transients or short circuits will lead to an accelerated breakdown of the weakened insulation.

In some cases (mainly DC-applications) conductive deposits on the outside of insulating parts have been observed. Such deposits distort the electrical field and will also lead to a breakdown.

How does corrosive sulfur look like?

In most cases copper sulfide deposits can not be detected by a simple inspection. The copper wire needs to be de-wrapped and the paper to be degreased in order to make visible the shiny deposits (Fig. 2).
In some cases the copper conductor can be dark or multi-colored. The discoloration can significantly vary within the length of the same conductor.

Diagnostic features

Gas-in-oil characteristics
Gas-in-oil analysis shows no deep changes and irregularities. The reason for that is that below an oil temperature of 150°C DGA does not really give serious indications, but those temperatures are high enough for developing corrosive sulfur. In some other cases there has been an increase of carbon oxide gases, indicating a higher service temperature.

Oil values
There is no significant change in the oil values as well. Nevertheless it is highly recommended to follow the DGA and oil characteristics on a regular basis in order to recognize possible irregularities early enough. Copper sulfide formation cannot be related to the amount of copper dissolved in oil.

Degree of polymerisation of paper
Paper from the affected units has been investigated for degree of polimerization. There were no signs for a strong paper ageing.

How can units at risk be identified?

The mechanism of copper sulfide formation is unknown. Oxygen radicals and electrical field seem to play an important role.
The application of corrosive oil for itself is not a sufficient argumentation for a unit to be classified as risky. Usually units at risk combine two or more of the conditions listed below. Since the mechanism and the factors influencing the copper sulfide formation are not fully known, there is a need for more field data, in order to classify the risk factors more precisely.

Equipment at risk may combine two or more of the factors listed below:

Corrosive oil
\+ **High service/ambient temperature**
\+ **Rubber bag**
\+ **Application of unvarnished wire**
\+ **Service conditions (transients, short circuits; maintenance procedures)**
\+ **Experience of the manufacturer**

Testing of an oil for corrosivity

Siemens supports the philosophy that testing methods should reflect the interaction between copper, paper and oil and should find a reasonable compromise between thermal, oxidation and corrosion stability.

The testing method proposed by Siemens has been evaluated in a Round Robin Test within CIGRE TF A2.32.01 and has been proposed for standardization. This test adopts a paper-wrapped copper conductor and transformer oil at 150°C for 72 h. Both the copper conductor and the paper strip are evaluated for discoloration and deposition (Fig. 3a and Fig. 3b).

Mitigation techniques for equipment considered to be in danger

Possible mitigation techniques evaluated up to now are:
- Oil Passivation and
- Oil change

Oil Passivation
The class of metal passivators consists of compounds on benzotriazole basis, which can react with the copper surface, thus protecting it (Fig. 4). This reaction, however, can be reversible under certain conditions. The most widely spread metal passivator with respect to the copper corrosion protection is considered to be Irgamet 39 (Ciba).
Metal passivators are not new. Benzotriazole compounds have been used widely in the lubricating industry, as well as in transformer oils, e.g. for decreasing the static electrification or improving the oxidation stability.

Investigations on the compatibility of Irgamet 39 (usual concentration of 100 ppm) with transformer oils show the following:
- Irgamet 39 does not negatively influence the oil dielectric parameters.
- the oxidation stability of the oil may be slightly reduced.
- some laboratory experiments showed a higher stray gassing tendency of the passivated oil. These results, however, haven't been confirmed in practice.
- Irgamet 39 is not stable under oxidative conditions.
- not all insulating oils have got an adequate response to the passivator.

Fig. 3a: Copper and paper strips after a test with not corrosive oil

Fig. 3b: Copper and paper strips after a test with corrosive oil

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The passivation should be carried out by experienced personnel using a dilution of Irgamet 39 in mineral oil. The oil passivation has the following main benefits and drawbacks:

Benefits	Drawbacks
Metal passivators stop the copper corrosion	Metal passivators can only prevent corrosion on copper but neither recover corroded copper, nor recover paper contaminated with copper sulfide
Metal passivators do not negatively affect the oil characteristics	The passivator is likely to be consumed by-and-by, therefore monitoring should be applied

The Siemens recommendation for the treatment of transformers/reactors affected from corrosive sulfur is:

- to consider the possibility of reducing the load and/or the oil temperature
- to add a metal passivator to a final concentration of 100 ppm
- to proceed with the regular oil supervision: monitoring of DGA, oil quality and passivator effectiveness.

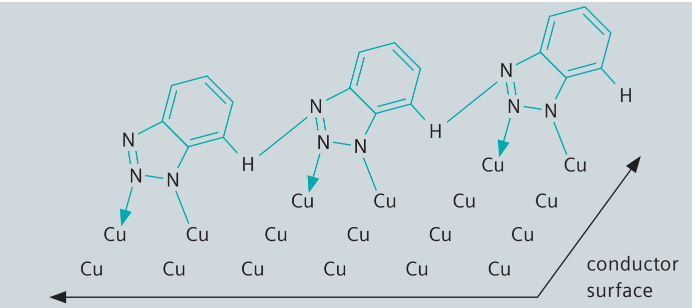

Fig. 4: A thin film of benzotriazole passivator on a copper surface

Changing oil
Another possible approach is the oil change. It must be guaranteed, however, that the mixtures of "old" and "new" oils are not corrosive. Oil change will also not be able to recover corroded copper and remove deposits on paper.

What should be done in the future?

A new oil specification with more stringent tests for corrosive sulfur is required. This will have a big impact on the oil types used up to now and it will be an evolution from a general to an application-oriented specification.
It must be considered, however, that natural sulfur compounds contribute to the intrinsic oxidation stability of mineral oils and are especially essential in case of uninhibited oils. They may, however, contribute to the copper corrosivity. A higher refining of the oil will remove sulfur to a high extent, but also leave the oil "naked", i.e. without protection against oxidation phenomena. In this case an addition of an oxidation inhibitor (e. g. DBPC di-t-butyl-p-cresol) is absolutely necessary in order to preserve the resistance of oil against oxidation.
This trend may lead to a noticeable increase of the application of highly refined inhibited oils in the future.

We will support you in any respect

If there is any concern of any of your transformers please refer to this bulletin and if you have any questions about Siemens transformers please contact your transformer representatives to enable us to give you the right support.

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