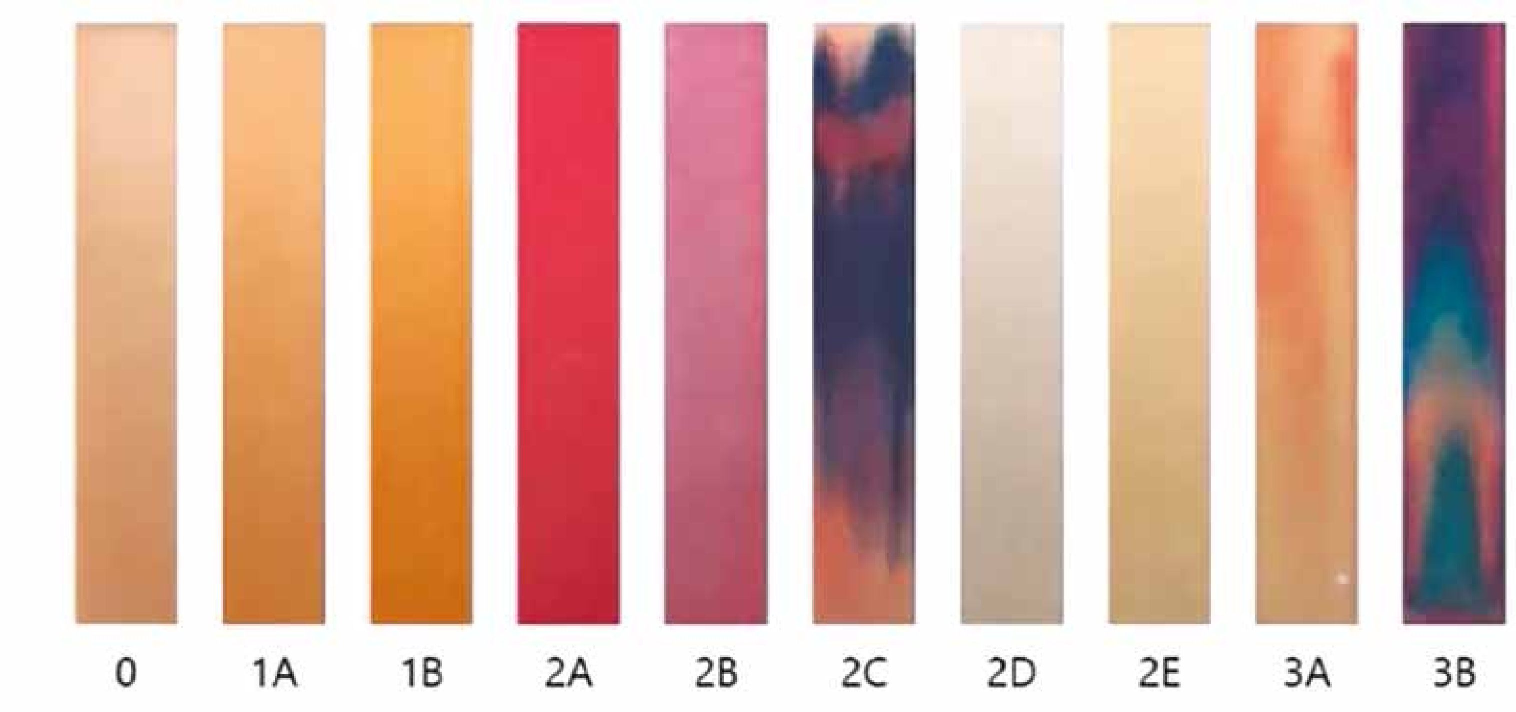
Sulfur corrosion phenomenon that damages copper inside a power transformer is quite old since it was observed almost immediately after implementing mineral oils a hundred years ago



ABSTRACT

Sulphur corrosion damages the copper of a power transformer, and it is commonly associated with mineral oil. Although the problem is quite old as it was noticed shortly after the implementation of the mineral oil for the transformers a hundred years ago, recently it received more attention. This complex topic is presented in the form of answers to the most common questions asked by users in practice. For example, why the test of oil for potential sulfur corrosiveness is required, what standards and tests are used today, how to mitigate the problem and avoid failure if the tests show that there is the sulphur corrosion potential, etc.

KEYWORDS

sulfur corrosion, copper corrosion, oil, tests, solutions

Sulfur corrosion phenomena

Tests, treatment, and consequences - Q & A

Sulfur corrosion phenomenon inside a power transformer is quite old since it was observed almost immediately after implementing mineral oils for insulating power transformers. The first papers on this subject appeared a hundred years ago [1]. The debate on how the sulfur in oil affects the copper inside transformers continues from that period on.

Sulfur is an abundant and important element that can be found in almost all natural materials on earth. It is the third most abundant element in the human body and all other living organisms. It appears in all crude oils since they originate from living organisms. Petroleum contains sulfur as well. According to [2], insulating oil contains a very large number of diverse organic sulphur com-

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pounds, even up to 20 %. The oil composition changes dramatically due to many different sophisticated processes, such as hydrogenation. Although there is early evidence of sulfur corrosion, it seems that this subject has become more popular and discussed extensively since 2005. Most of the transformer users, insurance companies and experts were concerned about this issue in the last two decades. With the appearance of new standards, the main guides for oil tests were revised, and sulfur corrosion tests were shifted from unnecessary to compulsory routine ones.

Since it has become a popular subject within the last two decades, it is necessary to reconsider the importance of this phenomenon. At the beginning of this millennium, the literature described many failed transformers due to sulfur corrosion phenomena. However, in the last few years, much fewer cases of failure have been reported, and most of the literature mainly describes deep research on different aspects of this phenomena.

If the industry aims to approach this phenomenon correctly and finds the adequate remedy to reduce the distress from the sulfur issue, it is recommended to bring back the sulfur corrosion tests as part of the special section in the main transformer oil testing process. Otherwise, it remains a very important unsolved threat for most of the transformers around the world.

In this article, I will try to answer the most common questions asked by transformer users regarding their concerns on tests, interpretation, and remedies. The questions, which are examples of the problems the users face, are followed by concise answers and discussion that explains the rationale.

1. Why do I need to test oil for potential sulfur corrosiveness?

Brief answer:

The most popular answers:

- I need to fulfil the demand from insurance companies.
- I have read a paper or listened to a presentation at one of the periodical conferences, which present many transformer failures due to this cause.
- One of the transformers in our company failed, and the postmortem diagnosis was a failure due to sulfur corrosion.

Discussion:

World transformer failure rate is approximately 1 % - 2 %. In some parts of the world, it is much higher, while in others it is as low as 0.5 %. Usually, the statistics of the failure do not drop below this value, despite the efforts to reduce the failure rate. It is quite impossible to eliminate all the transformer failure reasons. According to some statistics, the sulfur corrosion is responsible for up to 20 % of the annual failures, while other statistics show they are nonexistent. The postmortem diagnostics is not an exact science, because, in a failed device, the expert may observe many phenomena, including those that are not directly responsible for the failure. In most cases, the real failure cause is hidden by the transformer condition after the failure.

Insurance companies' demands are indeed very important but are less specific. For example, they do not specify the exact methods to test and actions to take. The users have two options: to perform only the tests required by the insurance companies or to do more tests trying to detect the potential sulfur corrosion.

2. Which tests or methods should I use to test my oils for sulfur corrosion potential?

Brief answer:

Perform as many tests as you may afford; the optimum is five tests related to sulfur potential corrosion:

- IEC 62535 [3]
- ASTM D1275, Methods A and B [4]
- DIN 51353 [5]
- IEC 62697 [6] and / or GC-AES method [7]
- IEC 60666 [8] for passivator content

Discussion:

These are the main standards for insulation oils but are not the only available methods to reveal these phenomena. Some organisations develop their own version as the Doble CCD. Which test is suitable or convenient for a specific transformer is highly dependent on original oil transformer specification, exploitation regime, ambient temperatures, importance to the grid, and many other specifics. If one performs more than one test for sulfur corrosion potential, it is quite common to receive different results. Even though the colour scale is

Figure 1. Isolated yellow native natural sulfur crystal

According to some statistics, the sulfur corrosion is responsible for up to 20 % of the annual failures

similar, the test conditions are very different. What increases uncertainty is the user choosing different labs, and thus receiving different conclusions. It was also found that the qualitative method is not consistent with the real transformer condition [9]. In this study, it is stated that all qualitative methods for detecting potential sulfur corrosion are about 80 % false positive or 100 % false negative. Some other experts do not agree with this statement and say the user should be aware that the results of existent tests are not clear and, in some cases, conform to all the results. The latest procedure is quite controversial, and it implies using the temperature of 150 °C for 48 and 72 hours to test oil for these properties. Those temperature values are very rare in normal or even heavy loaded transformers, and the effects on copper and cellulose due to the temperature stress in the tests may not reassemble any stress in real transformer operation. During the last few decades, the test standards became harsher, applying higher temperature for a prolonged time. Consequently, more oils were characterised as a cause of potential sulfur corrosion.

With all of this in mind, the final users must realise that the tests for potential sulfur corrosion may easily induce different diagnoses. Even if all the tests are in consensus, and the oil is indeed positive to all sulfur corrosion tests, it does not mean that the transformer is affected, or that any internal damage may be found. After more than 20 years of oils operating at high temperatures, it is much more plausible that the potential of sulfur corrosion will not be examined to its full extent. All those tests are mainly for finding if the oil may become corrosive in very specific and extreme circumstances.

3. The oil inside my transformer was found to be potentially corrosive to copper. How to mitigate the phenomena and avoid failure?

Brief answer:

Those are the popular option also by last CIGRE working group CIGRE 625, 2015 [10]:

- Passivate the oil
- Replace the oil
- Treat the oil and remove this corrosive property.

Discussion:

Those mitigation methods are the ones mentioned in the last CIGRE brochure from 2015, which describes all three techniques that only involve the oil, as shown in Fig. 2. The most popular technique is the passivation of the oil. Additional non-oil related strategies to mitigate the corrosion potential are to lower the transformer load and oil temperature, or simply: **"Do nothing".**

The mitigation oil techniques are known today to be quite problematic. Especially the passivation technique, that may induce harmful side effects such as a significant increase of tan Delta or dissipation factor of the oil (DDF). In many cases of new passivated oils, a significantly high value of DDF was observed, up to 10 times higher than the adequate limits for oil in service. In many cases, a large amount of dissolve stray gas in passivating oil was reported in different studies as summated in [10]. Passivators are also suspected to accelerate paper degradation. The literature mentions some cases of failed transformer nearly after the oil passivation process [7]. Passivation is probably the worst mitigation option, even worse than the **"Do nothing"** option.

Simple oil exchange option is either not an adequate option to remove the potential sulfur corrosion due to the fact that oil replacement is not a complete process. In the regular case, if 10 % of corrosive oil is mixed with 90 % noncorrosive oil, the mixture liquid is still corrosive [11]. Normally on-site, the oil inside the transformer may be replaced until the extension of 90 %. After oil exchange, it is still needed to passivate it as well. All the disadvantages of passivated oil reappear in this case after the efforts to replace the corrosive oil.

Oil reclaiming may be helpful in some cases but harmful in others. Instead, to remove corrosiveness, the oil may become even much more corrosive [12]. It is crucial to match the oil type, condition, and treatment. Otherwise, the damage may be significant again, or not effective.

No mitigation technique is capable of extracting the polar ion-containing copper or any other conductive compounds from the solid part of the transformer, especially the cellulose. The failure may occur immediately after passivation [13], but also, if the oil was replaced or treated, it will not change the fate of the transformer. The failure may occur due to significantly reduced electric properties of the solid insulation.

4. I choose to fill my new transformer with sulfur-free oil. Can I be confident that I will not have any internal corrosion issues?

Brief answer:

No. Sulfur exists in many other compounds and materials, and the corrosion mechanism may be initiated by other compounds beside sulfur.

Discussion:

Sulfur is one of the major raw materials for manufacturing most of the rubbers. Also, some varnishes, glues, and all other organic material inside the transformers, contain sulfur [11]. Noncorrosive oil may become corrosive in contact with some rubbers used for gasket or membrane [10]. Also, the insulating cellulose inside the transformer contains up to 20 % sulfur [11, 13]. The copper ions may also be dissolved in the oil by oxygen by producing CuO_2 [14], that may be absorbed in the cellulose and increase its conductivity properties. In addition, other metals inside the transformer or bushing are prone to corrosion by oxygen or even by some organic acid in the oil [15].

As described in [16], even coating the copper wiring is no guarantee that corrosion will not occur. In addition, an old study from 1960 shows that enamels are not able to resist at medium to elevated temperature. [17]

Perform as many tests as you may afford; the optimum is five tests related to sulfur potential corrosion. The different test may give different results

5. If sulfur is a common petroleum component, why do most of the cases seem to appear from 2000, why was almost nobody aware of this phenomenon before?

Brief answer:

The copper sulfur-corrosion-related failure exists because the insulating liquid can be found in electrical devices. From the beginning of the last decades of the last century, more failure appear as caused by sulfur corrosion. Most of the sulfur corrosion-related failure is an attribute to a specific compound dibenzyl disulfide (DBDS). Most of the research, since then is focused on the effects of this specific compound.

Discussion:

The phenomena of copper corrosion due to some sulfur compounds were observed 100 years ago [1]. By the end of the last century, it was very complicated to differentiate between the black residues due to sulfur corrosion, or carbonisation and sludge. Transformers failures were inspected, and most of the users and experts attributed the black deposits to oil oxidation products or carbonisation, mainly based on the postmortem stage of

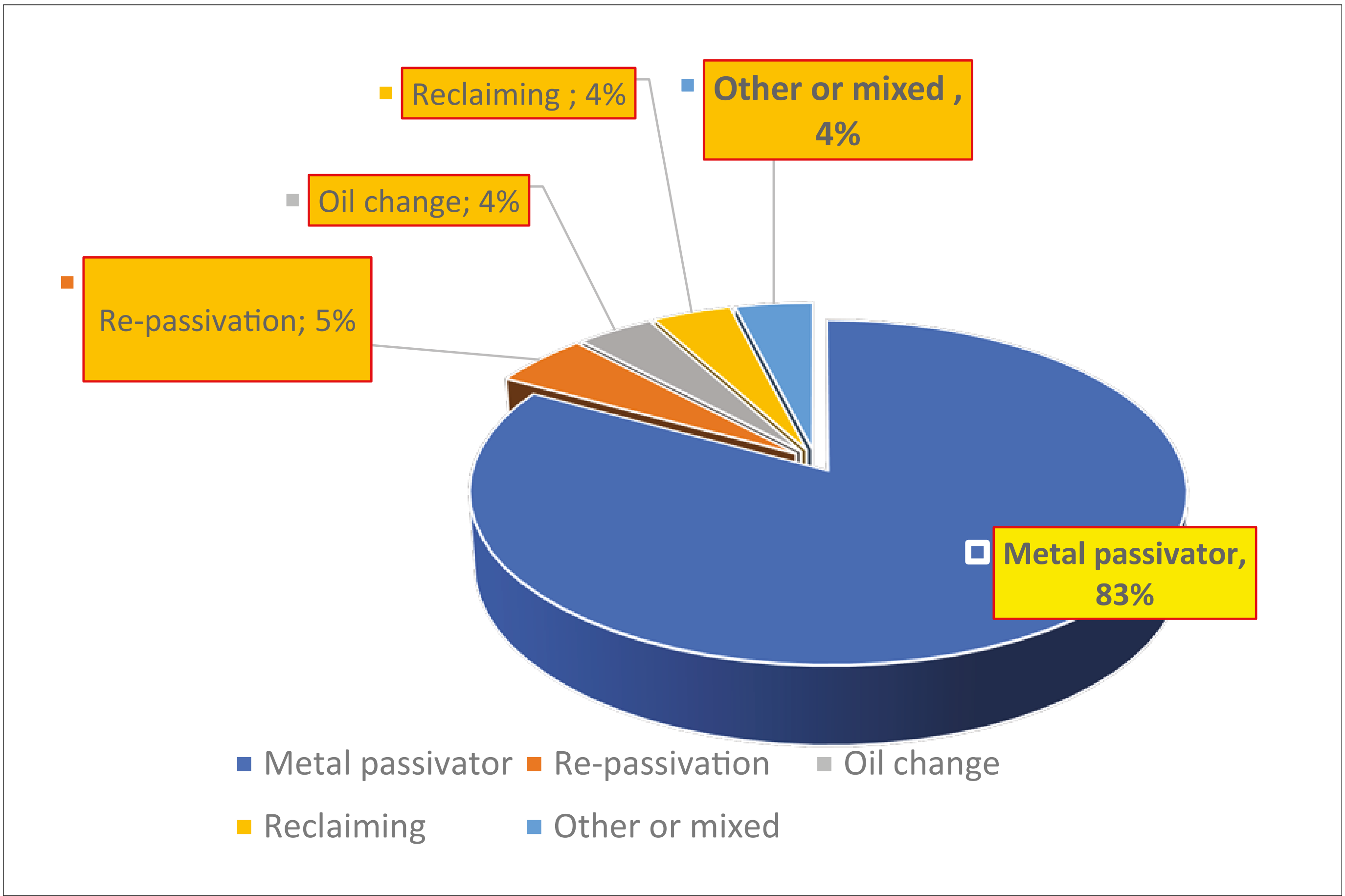

Figure 2. Mitigation methods according to CIGRE brochure 625 [10]

If the oil is found to be potentially corrosive to copper, the most common solution is to passivate the oil, but it also may be the worst one

the failed transformers. Without modern devices, such as scanning electron microscope (SEM), most of the users consider all-black paint on paper and copper originating from a hotspot or fire product, as shown in Fig. 3. This is also the case with Fig. 4 showing an old step-up transformer from 1960 that failed and only by the assistance of modern devices was it diagnosed as failed due to sulfur corrosion. Without modern tools, the engineers did not attribute the black spot to sulfur corrosion deposits. When Doble oil survey started to observe that some of the insulating oil became corrosive due to sulfur, [11] the results were correlated with the actual failures that had occurred. At the beginning of 21st century, Scatiggio et al. (7) succeeded in revealing one of the sulfur compounds that was found in many recently failed transformers due to sulfur corrosion. The origin of this substance DBDS remains arguable until today. Lately, other oil types and brands have been discovered that possess the same potential of being corrosive to copper, without the DBDS, but also became corrosive to oils and cause many failures [18]. The detection of the corrosive sulfur compounds responsible for the phenomena remains a task for the future. In the study [19] the possible pathway for this research is described.

Figure 3. Carbonated deposition during a fire and sulfur deposition due to corrosion by SEM

The cause for increasing abundance of copper corrosion-related failure is not only due to the more specific and accurate detection of the post mortem situation but also due to the strict economical transformer designs. In addition to the developments in the design software and models, the allowed temperature rises above the ambient were increased from 55 K to 65 K. This permits increasing the loading capacity for a strictly designed transformer.

Another important cause of the increasing numbers of transformer failure from 2000 is an important modification of the insulating mineral oil composition. For increasing the insulation properties, the total sulfur concentration was lowered significantly [20]. The oil became more suitable to higher voltages and higher temperature, but more prompt to oxidation and much more corrosive, especially at higher operation temperatures. Most of the organic-sulfur compounds expelled during the overrefining process were responsible for oxidation stability. The remaining sulfur species were susceptible to moderate to higher temperatures. Those temperatures were uncommon in the old designed transformer but became normal for newly designed transformers.

Even if the sulfur-free oil is used, that does not guarantee that the will be no corrosion issues

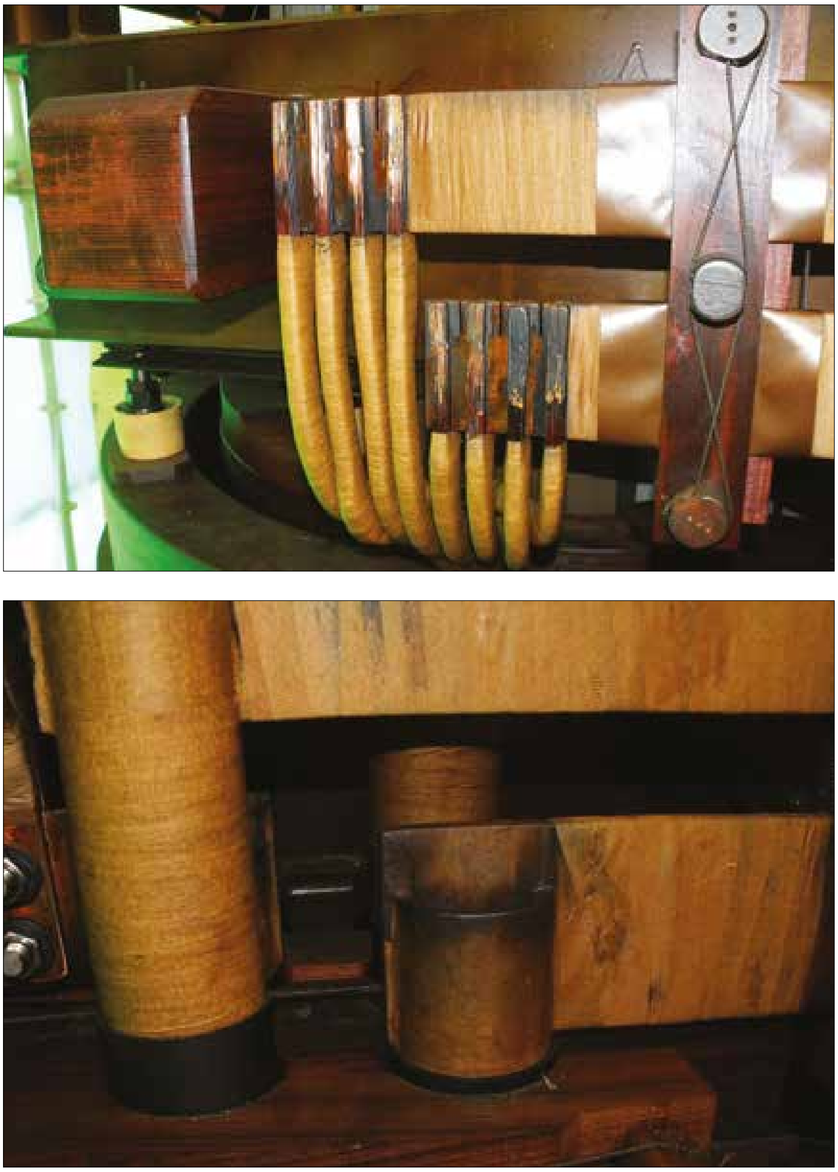

Figure 4. Sulfur corrosion phenomena for a step-up transformer energised with original oil since 1960

Conclusion

Copper corrosion mechanism by sulfur is not the only cause of corrosion inside the transformer, and the insulating liquid is not the only source of sulfur inside the transformer.

It is quite impossible or non-practical to try to completely avoid the sulfur or internal corrosion, during all the operational life of the transformers.

Among oil mitigation technique, the passivation is probably the worst one, even if in our days it is the most popular one. The proper mitigation technique has to be discussed and agreed between the transformer user and the expert who has to consider all the available tests and transformer data. Those recommendations have to be based on many factors, such as transformer importance, loading regime, grid needs, and many others. In some special circumstances, the passivation may be the preferred options, but probably not in most of the cases.

Only rarely is sulfur corrosion failure warned by routine tests, as shown in Fig. 5.

Normally, any routine oil or electrical tests are capable of detecting an incipient failure due to sulfur corrosion.

Tests for potential sulfur corrosion should not be performed only once, even if the first time it shows “Not corrosive”. The corrosion properties of the oil may be changed during its operational life.

The sulfur corrosion mechanism is not yet elucidated.

Any mitigation technique is not capable of reversing the process of copper damage and restoring the cellulose insulating properties.

The best way to minimise the effect of sulfur corrosion is to design the transformer with sulfur content as low as possible in all the internal parts, not only the oil, to reduce the average temperature as

The increase of the nominal temperatures in today's transformers compared to the old units is one of the reasons why the sulphur corrosion issues are more common today

much as possible, in order to avoid unusual hot spots inside the transformer. If one is interested in eliminating this phenomenon with any price, they may use very expensive conductive materials as gold or platinum, since those metals are not sensitive to corrosion phenomena of any kind. Using only "free sulfur" liquid does not provide any assurance of sulfur-free corrosion, even if the windings are enamelled. The low solubility of copper ions in the new oil brands may induce an increase in the number of ions absorbed by cellulose.

Until now, there have not been any single tests that may predict sulfur corrosion failures with 100 % confidence.

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Figure 5. DGA signal created by sulfur corrosion phenomena, ethylene reaches 750 PPM

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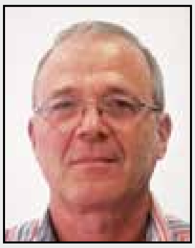
Figure 6. Disintegrated copper due to corrosion

Author



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He is also the author and co-author of many papers, CIGRE brochures and presentations at prestigious international conferences on insulation oil tests, focused on DGA, analytical chemistry of insulating oil and advantageous maintenance policy for oil and new transformers.