

Application of transformer

A technical review of how and why passivators work in transformer mineral oil and their effectiveness in retarding copper corrosion

Introduction

Since about 1996, the electric power industry has seen a rash of failures of large power transformers, shunt reactors, load tap changers and bushings due to conditions caused by corrosive sulfur compounds in electrical insulating oil. This was a worldwide phenomenon with the Brazil electric system being the most se-

verely impacted. The phenomenon is not new and has been known since the early 1930s. Up until the 2000 time frame, the failures due to corrosive sulfur were sporadic and manageable. However, from 2000 through 2007, the rash of failures was so prevalent that several utilities were concerned with reliability on their system. As a percentage of the total population of transformers the failure rate

KEYWORDS

passivators, benzotriazole, BTA, Irgamet 39, Irgamet 30, corrosive sulfur, copper sulfide, transformer oil, insulating mineral oil

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For the past 20 years corrosive sulfur in insulating mineral oil has caused a rash of failures of large power transformers, shunt reactors, load tap changers and bushings

passivators in insulating mineral oils

attributed to corrosive sulfur is still very small but impactful.

Transformers are large industrial machines that are basically handmade, take many months to build and cost millions of US dollars, are specific to a utility system and cannot be easily replaced. Transformers are designed and built to last 20 years or more at nameplate rating with many of them operating over 40 years. The corrosive sulfur failures in recent years involved relatively new electric apparatus, most less than 10 years old and some with less than a year in service. Spare transformer policies in place during the 1990s and early 2000s, as a result of utility deregulation in the

United States and other parts of the world, in some cases reduced available spares. Thus, replacements for failed transformers were not available and compounded the issue. Those policies have since been revisited and the amount of spare transformers available has been readjusted.

Transformers vary in size but large units can hold from 35,000 to 100,000 liters or more of electrical insulating oil and large

quantities of core steel, copper, electrical insulating paper and pressboard, among other components. The total weight of these materials can be several hundred tons when finally installed. None of these internal components were meant to be changed out over the life of the transformer. Failures of transformers due to corrosive sulfur compounds occur because they react with the copper conductor in the transformer windings, lead assemblies and silver components that

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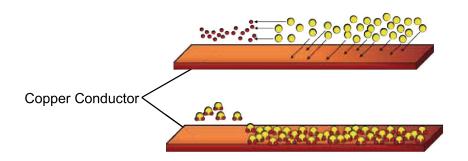


Figure 1: Corrosive sulfur attack of copper conductor and ions (red=copper; yellow=sulfur)

can progress into several different failure modes. Three failure modes are the most common.

The first are those that involve coating of conductors with a metal (copper or silver) sulfide film [1] (Figure 1). This film or coating is resistive compared to bare metal contacts and can result in their overheating.

Another potential failure mechanism is the result of a thick coating of the copper or silver sulfide flaking from the conductor into insulation structures.

The third is the formation of copper sulfide deposits in the paper insulation surround-

ing the copper conductor. Copper sulfide formed in the paper occurs when copper ions present in the paper react with the corrosive sulfur compounds in the oil and oil-impregnated paper insulation (Figure 2). The conductive copper sulfide causes a reduction in dielectric strength of the paper insulation. Failure results when the dielectric breakdown strength of the conductor insulation is exceeded by the voltage stress which can be influenced by transient voltages. The result is arcing between two or more strands or possibly disks [2].

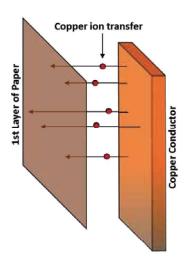
Another mechanism that produces copper sulfide deposits in the paper occurs where a dibenzyl disulfide (DBDS)-copper

complex forms at the copper surface, causing the dissolution of copper in that location. Researchers that formulated this mechanism suggested that copper sulfide formation on insulating paper via the DBDS-copper complex occurs at lower temperatures, usually 135 °C and below. When the decomposition of DBDS-copper complex occurs, copper sulfide is deposited and the radical intermediates (benzyl radical and benzylsulfenyl radical) are generated [3].

Sources of corrosive sulfur

There are a variety of sources of sulfur in a transformer, but not all sulfur compounds are corrosive [4, 5]. Electrical insulating mineral oil was at one time a major source. Electrical insulating mineral oils are refined from crude and as such contain a variety of undesirable nitrogen, oxygen and sulfur compounds. Depending on the refining technology and the crude source, most reactive sulfur compounds such as elemental sulfur, mercaptans, and some sulfide and disulfide compounds can be either destroyed, removed or converted. However, some corrosive sulfur compounds may escape degradation in this process or be produced as a result of the severe treatment.

Other sources may include materials of construction within the transformer such as gasket materials, glues, papers, and others. It has recently been determined that stable sulfur compounds in transformer oil such as thiophenes can be thermally degraded at temperatures



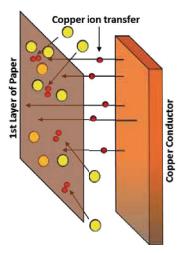




Figure 2: Mass transfer of copper to paper insulation (left); Corrosive sulfur compounds reacting with copper ions to form copper sulfide (middle); Corroded copper and copper sulfide on paper insulation (right)

99 Sources of corrosive sulfur in the insulating mineral oil are, as a result of undesirable sulfur compounds, those that can breakdown under specific conditions and reactive sulfur compounds that leach from the materials of construction in the transformer

in excess of 400 or 500 °C into corrosive species such as elemental sulfur [6]. One compound in particular, dibenzyl disulfide (DBDS), has been found to be corrosive under certain conditions and was present in many of the oils involved in transformer failures from 2000 to 2007. It has been reported that DBDS is not a naturally occurring substance in crude or normally present after refining [7].

Passivators and passivation

Remediation

Utilities were faced with trying to reduce their risk on transformers that possibly could be contaminated with corrosive sulfur. Two major approaches were developed early on with a third one following later. The early approaches were changing out all of the oil in the transformer and/ or passivating the oil. Changing the oil in a transformer is a costly endeavor and time consuming but is mostly complete with only 5 to 8 % of the oil containing corrosive sulfur remaining in the winding. Passivation is a process in which a chemical is added to the oil and binds with copper surfaces to form a boundary layer on the conductor so that the corrosive sulfur in the oil will not attack the copper. It should be recognized that corrosive compounds in the oil remain unchanged and are just held away from the conductor surface by this boundary layer. Passivation, which is used in other industries such as lubricating oils, was not a common practice in oils used in transformers where the oil is in service for decades. However, passivation can be done quickly and less expensively than other remediation efforts. As a result, passivation became widely used for corrosive sulfur remediation.

One major concern is that there is a population of transformers and reactors that are in service with oils that have excessive corrosive sulfur or a propensity to form it. Many of the failures seem to have occurred in that 2000 to 2007 time frame with

apparatus that had been in service from 1 to 7 years. During this window, the number of units with suspect oil that have been placed in service could represent a large monetary value even though it is a small percentage of the total units in service. Not only is there the cost of the apparatus, there is also loss of revenue and possible regulatory fines if power is not delivered as specified in contracts.

Although passivators have been around for a long time in the lubrication industry, their use is relatively new in transformers for the application of corrosive sulfur abatement. In this paper, the term "passivators" is used to describe compounds that bind with reactive metal surfaces, coating them and dissolved metals such as copper ions, and reduce their rate of reaction. This includes retarding oxidation reactions with organic compounds and reactions with corrosive sulfur. Passivators are composed of two basic types: sulfur based and nitrogen based. This paper deals with nitrogen based passivator compounds for these are the ones commonly used in transformer systems.

The first suggested use of passivators in transformer oil that the author is aware of was in 1954 by the Manchester Oil Company in the UK and also by the Shortland County Council in New South Wales, Australia in order to control oxidation, not corrosive sulfur [8]. In reality, it appears that the additive was really a com-

bination of a passivating compound (anthranilic acid) and an oxidation inhibitor (phenyl-B-naphthylamine) [8] that had a synergistic effect. In 1967, J.J. Melchiore and I.W. Mills of the Sun Oil Company [9] authored an article that dealt with the oxidation stability of transformer oils in response to accelerated oxidation tests such as the DOBLE PFVO (power factor valued oxidation) test. The results of the testing that they performed suggested that the use of a metal deactivator passivated the copper surface that was used as a catalyst in the experiment. The passivator decreased the catalytic effect of the copper and the amount of copper that dissolved in the oil. This reduced the oxidation of the oil and formation of deleterious byproducts. The passivator used was not identified, but it appears that it was not used in concert with an oxidation inhibitor. Some utilities in Australia continue to use passivators to control oxidation, whereas the use of them in the UK utilities was phased out and replaced with only oxidation inhibitors. Benzotriazole (BTA) has and continues to be used as a passivator to control streaming (static) electrification in large power transformers since the late 1980s, mostly by some transformer manufacturers in Japan.

Passivators currently used in electrical insulating mineral oils are primarily nitrogen based and have been predominantly benzotriazole (BTA) or similar chemistry. BTA is a granular solid at room temperature and requires heating and mixing to dissolve in the oil, so it is less desirable than oil soluble liquid based compounds. A triazole derivative, Irgamet 30 (produced by CIBA, now BASF) has a hydrocarbon molecule tail attached. The BTA derivative is liquid at room temperature and therefore much more readily mixes with transformer mineral oils. The one passivator that is primarily used for suppression of corrosive sulfur reactions is a tolutriazole derivative, Irgamet 39 (also produced by CIBA, now BASF), and is also oil soluble. The chemistries of each are shown in Figure 3.

Passivators, first used in transformers as early as 1954, are compounds that bind with reactive metal surfaces, coating them and dissolved metals such as copper ions, and reduce their rate of reaction

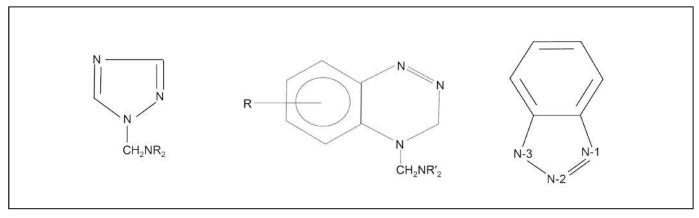


Figure 3: Common nitrogen based passivator compounds - Irgamet 30 (left), Irgamet 39 (middle), Benzotriazole (right)

Passivation is a process in which the nitrogen group of the passivator molecule chemically binds with the copper and other reactive metal surfaces with no physical change of the copper

Corrosive sulfur attacks the copper in such a way as to disrupt the copper surface and then complexes with it to create copper sulfide, thus in part becoming a permanent change. Passivation is a process in which the nitrogen group of the passivator molecule chemically binds with the copper and other reactive metal surfaces with no physical change of the copper. The passivator molecule is attracted to the metal surface and is held to the reactive site so that same site cannot be occupied (attacked) by a corrosive sulfur molecule. Passivator bonding is said to be 90 to 99 % effective on clean surfaces in oils where corrosive sulfur does not already exist. An XPS study determining the coverage of passivator on the copper indicated that the copper was not fully saturated even at a concentration of 100 mg/kg [10].

Passivator bonding to copper and other yellow metals is through nitrogen lone pair orbitals that forms a highly ordered copper-passivator polymer through strong charge transfer interactions between passivator molecules. Most research has shown that the passivation is a monolayer, is highly ordered and does not build upon itself (Figure 4).

The copper surface of a copper conductor has an oxide layer and thus is really defined as copper oxide (Cu2O). Under this configuration, this surface is consi-

dered to have Lewis acid-base site pairs, which means that is an electron pair acceptor. Researchers have shown that the most common type of chemisorption of the BTA molecule to the copper surface is the interaction of what is called the mid nitrogen to the copper cation (identified as position N-2 in Figure 3 for BTA). The chemisorption process is further stabilized by hydrogen bonding from the N-3 position (Figure 3 for BTA) to the oxygen anion on the copper surface. There is also hydrogen bonding between BTA mol-

ecules [11]. A depiction of the passivator chemisorption onto the copper surface was taken from Reference 11 and shown in Figure 5.

Anything that prevents the passivator from bonding to the copper surface will impact the coverage of the passivator. So, if copper sulfide formations have already developed then the passivator cannot attach to this area. Passivator cannot remove copper sulfide formations.

Presently, the current treat rates are:

- BTA: 20-30 mg/kg (ppm)
- Irgamet 30: 10-50 mg/kg (ppm)
- Irgamet 39: 100 mg/kg (ppm)

The effectivity of the passivator should be tested by using ASTM D1275B, and the Doble covered conductor deposition (CCD) test or IEC 62535 (CCD test).

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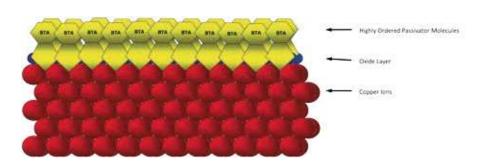


Figure 4: Diagram of passivator bonding to copper surface

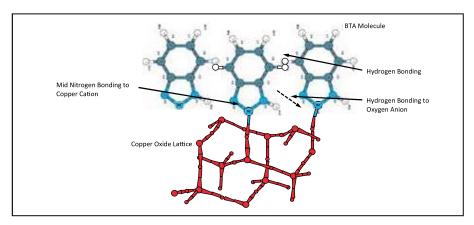


Figure 5: BTA chemisorption onto copper oxide lattice

There is a German method, DIN 51 353, which is sometimes used but it has been found not to be severe enough for the detection of corrosive sulfur and is no longer recommended. The addition of passivator is not always effective. Doble is aware of two cases in which the oil from a transformer which was passivated was tested via ASTM D1275B and failed the test. The addition of more passivator up to a concentration of 250 mg/kg did not solve the issue and the oil still failed the ASTM D1275B test. These types of results are rare and in most cases the passivation process is effective at least in laboratory tests, but it does illustrate the point of conducting laboratory tests to confirm the effectivity.

Care in adding the passivator is of importance as it needs to be mixed well within the transformer oil system. Some oil processing activities can remove the passivator. Simple dehydration or degasification of the transformer oil will remove a small percentage, but moving the oil through clay filtration media (Fuller's earth) will typically remove it all. The effects of filtering the oil through activated alumina or synthetic media are unknown.

Passivator molecules can also bind with free copper ions or particles present in the bulk oil. In effect, passivators and corrosive sulfur compete for the same reactive metal sites, along with other compounds (see Figure 6). It is believed that the passivator can absorb into the surrounding paper insulation setting up a dynamic equilibrium between the paper and the oil. The passivator in the paper will also react with the copper ions that have migrated to the paper from the copper conductor.

It should be noted that given the right cir-

cumstances, the passivation process can be undone (reversed). At high enough temperatures passivating compounds can be degraded and rendered ineffective although BTA appears to be more stable than Irgamet 39. Oxidation also renders passivation less effective. This might be due to degradation of the passivator or reduction of the active sites on the copper surface due to the formation of the oxide layer. As a result, constant monitoring of the passivator concentration is required as some transformer systems will consume it or degrade it rapidly, whereas in others it will stay stable for years. As transformers systems and their chemistries are complex, the stability of the passivator is hard to predict.

There is some research that shows that in other than transformer applications, where BTA is used to passivate a copper or copper alloy surface, there can be a concentration effect [12]. Because BTA and a corrosive sulfur compound are competing for the same active sites on the copper surface, if BTA concentrations fall below a certain concentration level, corrosive sulfur will overwhelm the passivator and corrosion of the copper surface will start to occur again [10]. The concentration at which this will occur is unknown and it is most likely related to the amount of corrosive sulfur available in that system. As the amount of corrosive sulfur is different in every insulation system, it would be difficult to assign a finite value.

Transformers have failed after passivation. The prevailing theory is that these units were passivated too late in their life cycle and the corrosive sulfur had already done its damage. This is likely true, but it is possible that the passivator layer can also be disrupted along the edges of copper conductor that has a rectangular shape. Figure 7 is a photograph of paper insulation in which copper sulfide has formed and a diagram of copper conductor that the paper surrounded. It is unknown if the passivator was not as effective at the edge, or if the corrosion reactions had already advanced too far for passivation to be effective in that location.

Whether this is influenced by electrical stress or is strictly a heating phenomenon is uncertain. The speed at which copper sulfide is formed is influenced by heat.

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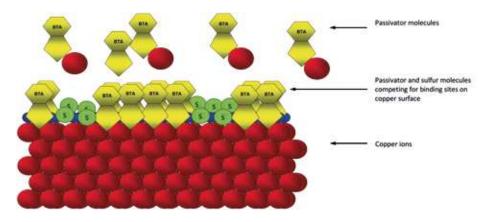


Figure 6: Passivator (BTA) and sulfur (S) competing for copper binding

99 Some transformers have failed after passivation

The higher the temperature, the more aggressive is the attack of the corrosive sulfur forming dissolved copper and copper sulfide. However, the case as described in Figure 7 is interesting as it shows copper sulfide deposits only on the top of the copper conductor and not the bottom, which shows a definite edge effect. The diagonal copper sulfide deposits going from left to right in the center of the paper in Figure 7 show that there is a slight gap where the deposits are fewer when compared to the deposits on each edge of the top of the copper conductor. It is known that there is a skin effect in transmitting AC through a conductor and that most of the electron flow is on the outside of the conductor [13]. In round conductor this skin effect seems to be equally distributed as described in the literature. The flow and distribution of electrons in a rectangular conductor might be different and thus the reason for the deposition pattern shown in Figure 7. This, however, would not explain why only the top edges of the copper conductor are affected and not the bottom edges.

Long term effects

The long term effects of the addition of passivator are unknown. In countries such as Australia and Japan, use of passivators to control oxidation of the oil or static electrification has had a relatively

long and successful history. These applications are different, however, than the one intended to control corrosive sulfur. Upon discovery of an oil with corrosive sulfur in a transformer, passivator should be added without delay so as to minimize corrosive activity as soon as possible. Passivator does not limit nor reduce the amount of corrosive sulfur in the oil, so if there is any degradation in the effectiveness of the passivator, corrosive sulfur will attack the copper. Some utilities have added passivator in the short term and then long term have made plans for removal of the oil, substituting it with an oil that is known to be essentially corrosive sulfur free or applying oil processing equipment that can remove certain corrosive sulfur compounds from the oil. Not all corrosive sulfur compounds are the same and some are less likely to be removed than others, so laboratory pilot studies should be conducted first in order to determine the effectiveness of such a process before it is performed on a large power transformer.

Removal of corrosive sulfur compounds by replacing the oil or oil processing is not total and some corrosive sulfur remains in the oil in the paper insulation, though it is significantly diminished. On average about 5 to 8 % of it remains. It is therefore recommended to add passivator to these units as well.

The concentration of passivator added to the oil can be stable or it can decline over time, and sometimes very rapidly, thus being the reason to monitor the concentration. Just from empirical evidence, it is usually recommended to re-passivate at the following concentrations:

- BTA: at 10 mg/kg (ppm) or below
- Irgamet 30: at 10 mg/kg (ppm) or below
- Irgamet 39: at 25 mg/kg (ppm) or below

Manufacturers of liquid filled electrical equipment, laboratories or entities that provide the passivating compounds may provide other recommendations than the ones provided above, and it has been reported that higher limits are being used. For example, 50 mg/kg has been reported as the minimum level for Irgamet 39, at which time it should be replenished.

Analytical methods

Several analytical methods exist to monitor the concentration of passivators. An HPLC method developed by Doble can be used to detect Benzotriazole and Irgamet 39. A similar method was developed by the IEC and the details are provided in IEC 60666. There are also some gas chromatography methods that can be used along with mass spectroscopy, but none that have become a standardized method

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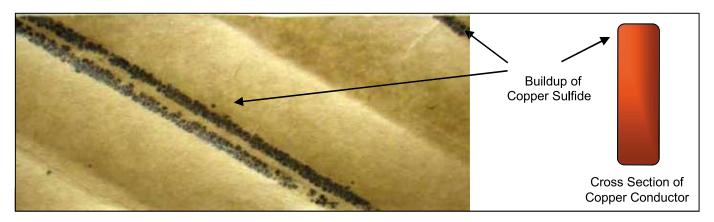


Figure 7: Copper sulfide deposits in paper of passivated transformer

as of yet. A method for the detection of Irgamet 30 has not been published.

Conclusions

Passivators bind with certain reactive metal surfaces to retard or delay attack by corrosive sulfur. They have been used in the past for other applications such as oxidation stability and control of streaming electrification. Passivators react with copper sites through lone pair orbitals and hydrogen bonding. As shown in Figures 1 and 6 and as discussed, passivation does not completely block all metal reactions with corrosive sulfur compounds. Passivation is a monolayer (single molecule thick) protection from corrosive sulfur. Passivators can be rendered ineffective through various processes and cannot remove copper sulfide that has already formed. Passivated transformers can and have failed, which may be due to: copper surfaces already attacked by corrosive sulfur and far along in the corrosion process, ineffectiveness of the passivator especially in oils with poor oxidation stability, degradation of the passivator or a higher affinity of the copper surface for corrosive sulfur as opposed to the passivating compound.

Transformers with DBDS in which passivator has been added should be tested not only for the passivator but the DBDS concentration as well. During formation of copper sulfide the DBDS is consumed. A reduction in DBDS concentration means that active corrosive sulfur attack is ongoing. Passivation should retard this process and the DBDS concentration should remain fairly constant. If the DBDS concentration continues to decline, then the passivator was not effective.

Passivators can be removed through certain oil processing activities, especially treatment with clay filtration media (Fuller's Earth), and thus may need re-passivating after such a treatment. The levels of passivator must be monitored in order to adequately protect the transformer or other liquid filled electrical apparatus.

Further research is needed to determine if passivation is a good long-term solution for in-service oils with excessive amounts of corrosive sulfur. Transformers considered at risk should be passivated or remediated with a more extensive treatment.

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