# Passivators – What They Are and How They Work

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In the past several years there have been some failures of very large power transformers and shunt reactors associated with the presence of corrosive sulfur in the transformer oil. This problem occurs despite the fact that the oils involved have passed standard specification test criteria for corrosive sulfur, such as ASTM D 1275. These failures occur because corrosive sulfur in the oil reacts with copper to form copper sulfide, a conductive compound. The copper sulfide can form at the copper surface or with copper ions in the oil and paper. Some of the copper sulfide formed at the copper surface can also migrate to the paper insulation. The formation of copper sulfide is depicted in Figure 1. 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 turns or possibly disks [1]. Information about corrosive sulfur has been presented in this publication previously [2,3, and 4].

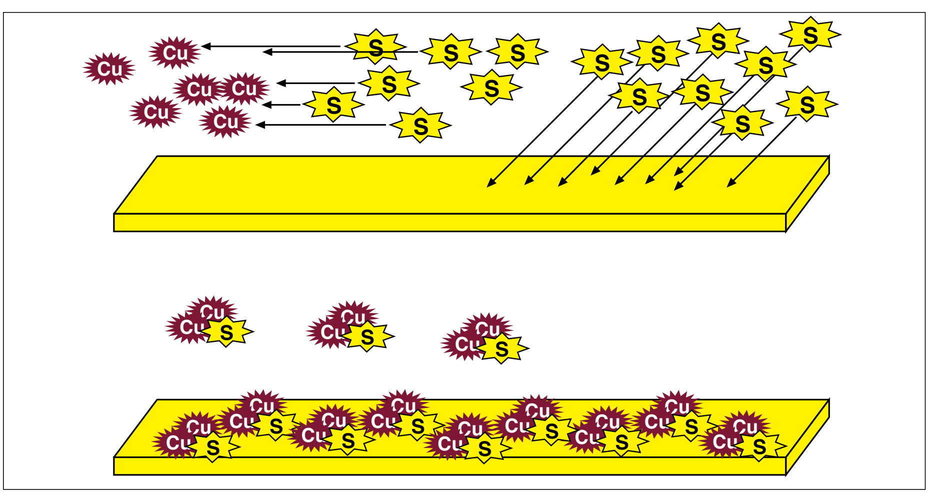


**Figure 1 — Corrosive Sulfur Attack of Copper Conductor and Ions (Cu=Copper; S=Sulfur)**

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 the past few years with apparatus that has been in service from 1-7 years. During this window of time, 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.

This concern about corrosive sulfur has led several transformer manufacturers and oil refiners to recommend the use of passivators by adding them to the oil. There are different kinds of passivators that can be used, but one that has been recommended for the corrosive sulfur problem is added to reach 100 ppm (mg/kg). This would mean that in a 10,000 gallon transformer, 7.5 pounds of this passivator would have to be added to the oil to make the final concentration 100 ppm.

So what exactly are passivators? Although passivators have been around for a long time in the lubrication industry their use is relatively new in the electrical industry. Passivators, also know as metal deactivators, react with reactive metal surfaces and dissolved metals such as copper and silver and reduce their rate of reaction with compounds in the oil. This includes oxidation reactions with organic compounds and reactions with corrosive sulfur. Passivators are composed of two basic types, sulfur based and nitrogen based.

The first suggested use of passivators in transformer oil of which the author is aware was in 1967 by J.J. Melchiore and I.W. Mills of the Sun Oil Company. The article that they wrote [5] 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 (passivator) coated 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 by-products. Passivators have been used in some cases for this purpose. Passivators have also been used by some transformer manufacturers in Japan for static suppression.

Passivators that have been used in electrical insulating mineral oils are nitrogen based and have been predominantly benzotriazole (BTA) or its derivatives. BTA is a granular solid at room temperature and requires heating and mixing to dissolve in the oil, so it is less desirable than its derivatives. One type of BTA derivative has a hydrocarbon molecule tail attached. The BTA derivative is liquid at room temperature and, therefore, much more readily mixes with transformer mineral oils. One passivator that has recently been suggested for use for suppression of corrosive sulfur reactions is that produced by CIBA named Irgamet 39. There are several other manufacturers and brand names of products that are commercially available.

The action of the passivator is to have the nitrogen group of the BTA molecule bind with the copper, silver and other reactive metal surfaces. This process is a chemical bonding that, given the right circumstances, can be undone (reversed). 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 molecules can also bind with free copper and silver ions or particles present in the bulk oil (see Figure 2). In effect, the BTA and corrosive sulfur compete for the reactive metal sites, along with other compounds.

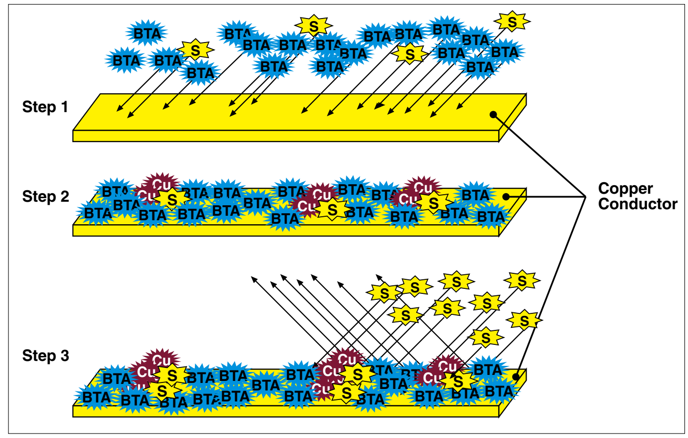


**Figure 2 — Action of a Passivator**
**(BTA = BTA or its derivatives)**

Much of the study on the use of passivator for control of corrosive sulfur reactions to date has been in the laboratory. The long-term effectiveness for retarding the action of corrosive sulfur in apparatus is not known. Investigations at the Doble Laboratory have shown that passivators retard reactions of metals with corrosive sulfur. However, even at moderate temperatures (110°C) with passivator added, under certain laboratory conditions corrosive sulfur attack still occurred. The reactions occurred over extended periods compared to experiments without passivator as copper sulfide was eventually observed on copper surfaces. The question is whether the passivator sufficiently retards the corrosive sulfur reactions so they are not of concern for the normal life of the apparatus. Once copper sulfide is formed on copper surfaces and deposited in the paper insulation, it is not removed by passivator or other means. The passivator undergoes a variety of reactions in the apparatus and can be degraded or consumed and might need to be added periodically to retain sufficient binding on the copper surface to block the corrosive sulfur reactions.

## Alternative Approaches

For new oils the best approach is to use an oil that does not have significant amounts of corrosive sulfur compounds as shown by passing a more rigorous modified version of the ASTM D 1275 corrosive sulfur test. Doble recommends performing the test at 150ºC instead of 140ºC and for 48 hours rather than 19 hours and using better nitrogen purging and sealing of the test vessel. In cases where oils have been used that do not meet this more stringent criteria, passivator could be used to retard further corrosion. An alternative approach is to use full or partial retrofills of the oil with an oil that does not have significant amounts of corrosive sulfur compounds even when exposed to very high temperatures. This can be tested on a case by case basis to determine the required dilution. All these methods deserve further research to determine the best long-term approaches to solving the corrosive sulfur problem.

## Conclusions

Passivators are metal deactivators that bind with certain reactive metal surfaces to retard or delay attack by corrosive sulfur. Passivators act by blocking the sites for corrosive sulfur compounds to attack the copper and form copper sulfide. As shown in Figure 2 and as discussed, passivation does not completely block all metal reactions with corrosive sulfur compounds. Further research is needed to determine if passivation is a good long-term solution for in-service oils with excessive amounts of corrosive sulfur.

## References

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