Stop Corrosive Sulfur:
A Successful, Multi-Directional Approach

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Abstract:
Corrosive Sulfur in transformer oil has been the cause of high-profile transformer failures in recent years. Oil treatments consisting of copper passivators have been only partially effective. Soltex has discovered a multi-step method that has been proven to change oils with corrosive sulfur into non-corrosive status, as well as significantly slowing oxidation and ageing of insulating oil and paper. This paper outlines the history of the problem as well as the research that led to the successful commercial launch of a product known as Soltex Sulfur Inhibitor.

Background:
Corrosive sulfur has recently received a great deal of attention by owners of power transformers. Before the mid-1990s, however, it was considered a phenomenon that occurred only with transformer oils of questionable quality. The consensus was that if one used one of the major brands of oil that this problem would rarely be encountered.

Many things have changed in the last two decades, however, to make the problem of corrosive sulfur a very real one:

1. Refining and oil purification methods have changed.
2. The transformer oil industry has seen many oil suppliers leave the market, shifting market share to new suppliers.
3. Sources of crude oil have changed; new sources contain different profiles of naturally occurring sulfurous compounds.
4. Transformer operating conditions and designs have changed. Today's transformers are designed with less cooling oil with respect to the mass of metal available, which raises the relative level of metal ions in the oil.
5. Modern transformers, too, are being operated at higher temperatures, which has several effects.
    a. Higher temperatures seem to have the effect of changing a type of sulfur from non- or poorly reactive one into a type that is more highly reactive.
    b. Higher temperatures drive chemical reactions to occur at a faster rate which means that the dissolution, reaction and plating effects of sulfur-metal compounds occur much more quickly than it would have in the past.

Types of Sulfur Compounds

Not all sulfur compounds in oil are harmful. Some are not only stable, but actually have antioxidant effects. Others, such as mercaptans, simple sulfides and elemental sulfur are highly reactive. Dibenzodisulfide (DBDS) is thought to be one of the more reactive sulfur species that is found in transformer oils. The types and quantities of sulfur in an oil depends on the source of the crude oil and the refining methods used. Different crude oils have different amounts of each of these sulfur compounds. Different companies' refining processes can remove or change sulfur compounds from one type to another.

What Happens with Corrosive Sulfur?

Inside a transformer, metals – copper, iron and aluminum, slowly dissolve into the transformer oil. Because of its molecular structure and properties, copper is the most easily dissolved and the most reactive of the metals normally found in transformers. Metal ions in solution combine with sulfur compounds to produce a range of copper-sulfur salts. The exact profile of the metal-sulfur salts that are created depends on the conditions inside the transformer, the types of copper that are present, and the types of sulfur that is present in the transformer oil.

But copper isn't the only metal that can take part in chemical reactions. The different alloys of aluminum and iron that are found inside a transformer also dissolve into transformer oil, and their ions can and do interact with sulfur. If copper isn't present, aggressive sulfur will combine with these other metals to form a variety of sulfur-metal salts.

These sulfur-metal salts, whether they're from copper, iron, or aluminum, saturate the transformer oil. When the concentration of salts reaches a certain point (which varies, according to the chemistry of the oil and the conditions in the transformer), the salts will grow in a crystalline structure on other surfaces inside the transformer. These surfaces may be paper, wood, or any surface that can act as a substrate to the growth of copper-sulfur, ferro-sulfur, or alumino-sulfur salts.

This process repeats itself [1] until the source of metal or sulfur ions is used up. Before this happens, however, the transformer will often experience problems because the metal-sulfur salts that are being deposited ("plated out", in common terms) are conductive. The buildup of these conductive salts leads to transformer failure.

What can be done about this? Studies have shown that sulfur is difficult to remove from transformer oil. Filtration with fuller's earth or other ion exchange media has very little effect on the concentration of sulfur compounds, although it can remove some of the metal-sulfur salts that are already in solution.

The Traditional Approach
Historically, corrosive sulfur has been dealt with not by treating the sulfur, but by hindering copper ions from entering solution. This can be done by using a variety of "Yellow Metal Passivators". These Yellow Metal Passivators, such as benzotriazole, or tolyl-triazole, form a very thin, non-reactive coating on copper and thereby slow its dissolution into transformer oil.

There are three problems with attempting to stop corrosive sulfur with the simple addition of a yellow-metal passivator, however.

1. There are several different alloys or varieties of copper and brass materials in every transformer. Each different type reacts differently with different copper passivators. Some are very well protected by one chemical passivator, but not another. Some don't bind well to either type.
2. Different iron, steel and aluminum metals are present in transformers, and they are also are reactive to aggressive sulfur. While they're not as reactive as copper, they do combine with sulfur and have a hand in the plating reactions that occur. Copper passivating chemicals – benzotriazole and tolyltriazole - don't protect transformers from reactions involving iron, aluminum or steel.
3. Copper passivators, by themselves, don't do anything to reduce the corrosive sulfur compounds in transformer oils. They simply attempt to intervene in the dissolution of certain metals. The underlying corrosion problem is still present.

Physical Removal of Sulfur:
Several attempts have been made to find a way to physically remove sulfur from transformer oil. Sulfur is very difficult to remove, however, from existing transformer oil. Filtration with fuller's earth or other ion exchange media has very little effect on levels of sulfur found in oil.

Chemical Removal of Sulfur:
Research at Soltex has found that aggressive sulfur compounds in transformer oil can be changed by introducing them to one of several reactive "sulfur scavengers". These compounds "tie up" sulfur in oil, preventing its reaction with any metal ions. The sulfur-metal salts are effectively prevented from forming, so they can't "plate out" onto cellulose insulation.

These sulfur scavengers are large, complex molecules that are especially reactive to corrosive sulfur compounds, but not to other chemicals found in transformer oil. They effectively combine with reactive sulfur and hold it in suspension, preventing it from combining it with metal ions in oil. Analysis has shown that some of the more aggressive types of sulfur, such as dibenzodisulfide (DBDS) can actually be changed to a less aggressive compound of sulfur.

Relationship Between Corrosive Sulfur and Oxidation:
Field and anecdotal evidence describes a correlation between low oxidation resistance of an oil and its propensity to develop problems with corrosive sulfur, given the same application conditions. While the basis for this correlation is not well understood, it has been noticed and discussed at CIGRE and IEEE and was considered significant enough to take into account during this investigation.

Commercial Development and Application:
In 2006 and 2007, continuation of this research program resulted in the development of a commercially available product to protect transformers from corrosive sulfur in transformer oil.

This new sulfur protection and reduction scheme protects transformers in three different ways, which work in a synergistic manner:

1. First, Soltex Sulfur Inhibitor uses a blend of several different metal passivators. Our research has found that a mixture of metal passivators are much more effective at preventing dissolution of copper into oil than a single compound. A years' worth of study and laboratory testing yielded precise ratios for the use of different metal passivators that would prevent the different chemicals from interfering with one another, and to work together to protect the maximum number of types of copper metals found in transformers.

2. Second, Soltex exploited the causal link between oxidation stability of paper and oil and the ability of the sulfur-metal interaction to proceed. It is our understanding and belief that oils that have lower stability against oxidation are more likely to promote the dissolution of metal and its reaction with aggressive sulfur compounds. For this reason, the product that we developed contains a powerful blend of different antioxidant chemistries that protect oil and paper from accelerated ageing and inhibits their ability to enter chemical reactions.

Third, Soltex developed a mixture of sulfur scavenging and passivating compounds. These chemicals seek out corrosive sulfur in oil and bind with it to prevent its interaction with metals, paper, or oil. The bound sulfur is effectively rendered harmless. The concentration of the most reactive types, such as DBDS, is actually lower after treatment with Soltex Sulfur Inhibitor. This goes far beyond the protection provided by simple yellow metal passivators.

Taken together, these three mechanisms have been proven to be very effective in protecting metals and reducing the amounts and types of corrosive sulfur compounds found in transformer oil.

Laboratory Testing:

ASTM D1275b Corrosive Sulfur in Oil Test:

Soltex Sulfur Inhibitor was first tested with four different oil samples that tested positive for corrosive sulfur. ASTM D1275B, which is the standard ASTM test for Corrosive Sulfur. This test measures the effect of subjecting clean copper strips to the oil being tested. We tested oil samples before and after treatment with Soltex Sulfur Inhibitor. The oil samples were provided by different independent laboratories and the analyses were performed at a major independent laboratory.

Sample 1 Test result:
Untreated sample: 4b
Corrosive Treated Sample
3a Tarnished

Sample 2 Test result:
Untreated sample: 3b
Tarnished Treated Sample
3b
Tarnished

Sample 3 Test result:
Untreated sample: 4c
Corrosive Treated Sample
3a Tarnished

Sample 4 Test result:
Untreated sample: 4b Corrosive
Treated Sample No Change (no corrosion or tarnish)

<u>In each of the samples that had "Corrosive" status, Soltex Sulfur Inhibitor changed the sample to "non-corrosive" status.</u>

Dibenzo Disulfide (DBDS) Testing:

Dibenzo Disulfide is a chemical found in transformer oils that has been linked to corrosion of copper and other metals. Reduction in Dibenzo Disulfide (DDS) content of the oil is considered to be very closely linked to reduction in corrosive behavior.

Four samples of oil were treated with Soltex Sulfur Inhibitor. <u>Of these four, there were significant reductions in the concentration of Dibenzo DiSulfide.</u> Some samples showed a greater reduction than others, but taken as an average, Soltex Sulfur Inhibitor lowered the concentration of Dibenzo DiSulfide (DDS) in the oil samples by an average of 14250 ppb, or 26% of the DDS concentration of the pooled samples.

Field Application:
Since its commercial introduction, Soltex Sulfur Inhibitor has been used in transformers (GSUs and substation units of several types) of varying ages and sizes. Results of oil tests on treated transformers have shown significantly lower dibenzo disulfide levels, lower oxidation rates, and enhanced protection for oil and paper. Transformer oil samples that have been tested have indicated that they are "non-corrosive" status.

Application Example:

A Chinese utility had two power transformers (Panyu 150 kV, 80 MVA) with oil that was extremely corrosive when tested with DIN and ASTM tests. A small sample of the oil was treated in the laboratory with Soltex Sulfur Inhibitor, which rendered the oil "non-corrosive". The utility then decided to treat both transformers with Sulfur Inhibitor. After treatment, the oil in both transformers tested "non-corrosive".

Soltex performed a full analysis on the oil from these transformers, before and after treatment. Analysis of the oil showed that the concentration of several corrosive sulfur compounds had been reduced or eliminated. For example, the concentration of 1-methyl dibenzothiophene had been reduced by 82% in one transformer and by 92% in the other.

How is Soltex Sulfur Inhibitor used?
The completed Soltex Sulfur Inhibitor is a pre-mixed, liquid concentrate blend of advanced passivators, oxidation inhibitors and sulfur scavengers and stabilizers.

It is added directly to transformers where there is corrosive sulfur or low oxidation inhibitor content.

Because Soltex Sulfur Inhibitor is a liquid, it is simply added to a de-energized transformer. No further mixing or blending is required. As delivered, Soltex Sulfur Inhibitor is dried, degassed, and highly processed. It is compatible with all brands of standard mineral oil and fire resistant petroleum oils.

Soltex Sulfur Inhibitor is made for field application in transformers that are filled with standard mineral oil. Soltex Sulfur Inhibitor is added to transformer oil to inhibit and prevent corrosion, plating, or other problems caused by corrosive sulfur.
Although it has a blend of advanced antioxidants, sulfur inhibitor is not made to slow or reverse problems of "gumming", polymerization, or premature oxidation of soybean oil dielectric fluids.

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