UNDERSTANDING CORROSIVE SULFUR PROBLEMS IN ELECTRIC APPARATUS

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ABSTRACT

Corrosive sulfur in oil has become a problem in electric apparatus. The problem is complex but recent investigations are providing a better understanding to help avoid problems in the future. Test methods for oils are being developed and there is some evidence that power factor measurements might be helpful in detecting deposition in apparatus. Mitigation methods for existing and developing problems are under investigation.

INTRODUCTION

There have been a number of failures of very large power transformers and shunt reactors associated with corrosive sulfur in electrical insulating mineral oils. Although the number of failures has been relatively small, perhaps 100 or so units, the assets lost have been substantial. The extent of the problem has not been determined, as test methods are just being developed to detect evolving problems for in service equipment. Examples have included the failure of numerous 500 kV shunt reactors, a 450 MVA autotransformer, and several large generator step-up transformers of the same design. The problem tends to develop undetected in the apparatus over several years before failure occurs. As a result there is some concern that the number of failures could grow considerably unless actions are quickly taken by the industry. Problems have been reported from many countries. Shunt reactor failures in Brazil have been especially troublesome, as several units have failed on the same transmission line.

These failures have occurred even though the oils, in most or all cases, passed internationally recognized industry specifications at the time for the corrosive sulfur test including ASTM D 1275A or DIN 51353. The problem occurs because the corrosive sulfur reacts with copper conductors (FIGURE 1) and silver contacts, to form metal sulfides that contaminate the insulating paper [1]. This section of the high voltage disk was from a transformer that failed after four years of service. Since the metal sulfides are conductive, the dielectric breakdown strength of the paper is reduced. Under some conditions, a breakdown occurs through the insulation between conductor strands on a disk or between disks (FIGURE 2). This ultimately leads to the failure of the apparatus. Another failure mechanism is the flaking of copper sulfide from the conductor that then bridges across electrical insulation.

Evidence of Copper Sulfide, Purple, Green, Blue and Grey Discoloration of Conductor
FIGURE 1

Evidence of Discharge Activity on Disk from Failed Transformer
FIGURE 2

APPARTUS AT RISK

So far the problems with corrosive sulfur have been mostly with larger power transformers and shunt reactors. This is likely for a number of reasons. The problem starts with copper conductors that are paper wrapped for insulation. Lower voltage apparatus have an advantage if the copper conductors are coated with enamel insulation. The enamel creates a barrier preventing reaction with the corrosive sulfur. The problem has been greater in warmer climates where there often are more consistently high operating temperatures. Corrosive sulfur problems are both time and temperature dependent. The longer an apparatus operates at higher temperatures, the greater the corrosion and formation of metal sulfides. Sealed transformers are more susceptible to the corrosive sulfur problem, as it is believed that oxygen reacts with copper and organo-metallic compounds competing for reaction sites with the corrosive sulfur. This slows down the formation of the conductive metal sulfides but does not stop their formation. Further, sealed transformers tend to be designed to operate at higher temperatures, about 10-15°C higher than units with free breathing conservators. There often are design and material considerations as well with units that operate at higher temperatures. There might be other reactions involving oxidation and corrosion that are not fully understood that could also be effected by the availability of oxygen. The amount of oxygen present is dependent on the amount of residual air after installation, air ingress through the oil expansion system and leaks, and consumption by the aging process.

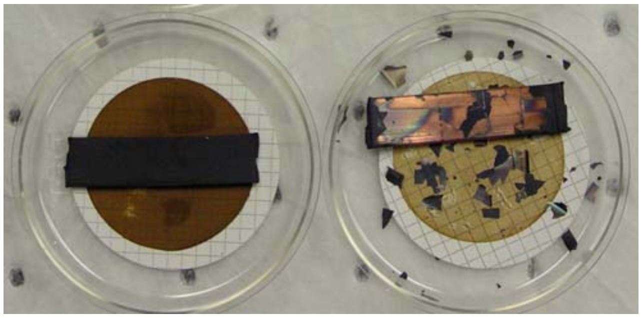
Corrosive sulfur problems were first recognized in the early 1900s in the United States. Methods to detect corrosive sulfur in oil were improved at that time and have been effective for many decades. It appears that in recent years changes occurred that have gone undetected, as oils continued to meet specifications but problems have occurred. It appears that the margin or temperature at which corrosive sulfur begins to form has been reduced for some oils. The following units have been identified as the most susceptible although corrosive sulfur problems has occurred in other units that do not meet these criteria:

- Sealed units (gas blanketed, sealed conservators, etc.)
- Units that operate at higher sustained temperatures such as generator step-up units
- Oil that has the propensity to form corrosive sulfur compounds (not to be mistaken with oils that have a high sulfur content), especially some oils from the past 5-10 years
- Kraft paper insulated transformers (as opposed to varnished or enameled wire -of less significance if thermally upgraded Kraft)
- Design considerations – localized overheating, high stresses

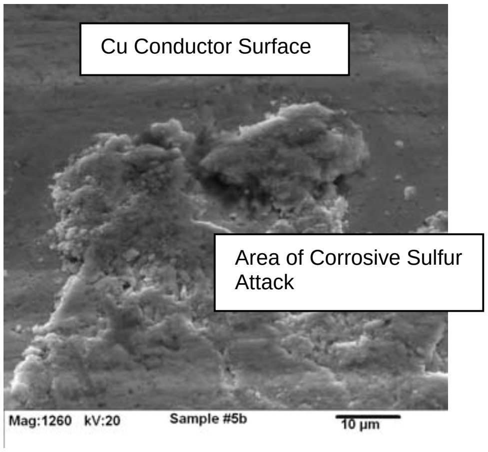
TRANSFORMER FAILURE MECHANISMS INVOLVING CORROSIVE SULFUR

There are really two distinct failure mechanisms that can occur individually or in concert with each other. Corrosive sulfur attack of copper or silver will form copper or silver sulfide on the surface of the metal. As the sulfur builds up and layers, metal sulfide flakes can start to fall off the surface and possibly into insulation in high stress areas where a dielectric failure can occur. FIGURE 3 shows a copper strip heavily contaminated on the left. The copper strip on the right is at a later stage in which the copper sulfide material starts to flake off the copper. The shiny under surfaces of the flakes is copper that has come off the strip with the copper sulfide. FIGURE 4 is a scanning electron micrograph (SEM) of a copper surface that is starting to be attacked by corrosive sulfur.

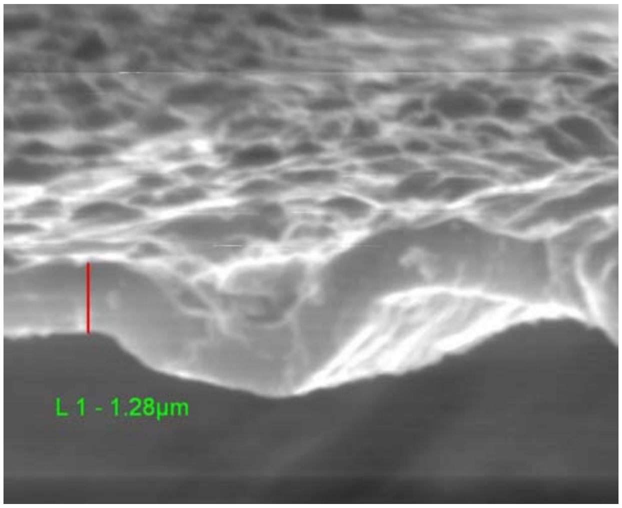
A closer look at the copper sulfide flakes (a conductive particle) actually shows copper sulfide that forms and compact on the surface causing the copper sulfide (Cu_2S) layer to thicken. This buildup process continues until a Cu_2S flake detaches from the surface and falls into the bulk oil or to insulating materials. The thickness of these detached flakes can be as small as 1-2 microns (FIGURE 5), but flakes up to 8 microns thick have been measured (FIGURE 6).



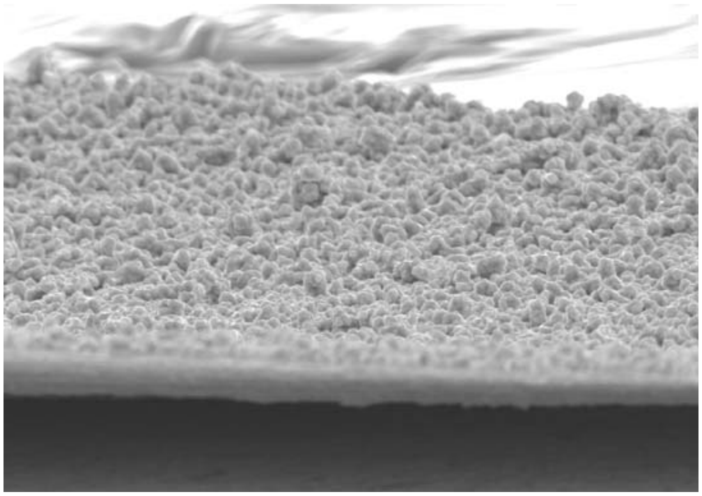
Copper Sulfide Flaking
FIGURE 3



Magnified View of Corrosive Sulfur Attack on Copper
FIGURE 4



Flake of Copper Sulfide, 1 Micron
FIGURE 5



Thick Copper Sulfide Flake, 8 Microns
FIGURE 6

The second mechanism appears to be the cause of most of the recent rash of failures. It is believed that over time, particularly at warmer temperatures, corrosive sulfur in the oil or sulfur compounds that become corrosive reacts with copper, silver and other reactive metals to form metal sulfides. Most of the sulfides are formed with copper. Although the mechanism is still unclear, it appears that the copper sulfide is formed on paper in two ways. One is by reactions of soluble copper or copper compounds with sulfur compounds on the paper layer surfaces that then continue to grow on themselves. The other is by deposition from the metal surface over to the adjacent paper surface in close contact with it. The copper sulfide causes a reduction in the dielectric breakdown strength of the paper, which if sufficient, can result in arcing between two or more strands and a subsequent burn through dielectric failure as is shown in FIGURE 2 [2].

There have been a number of failures where there is clear evidence that corrosive sulfur has played a very significant role and is probably the major causative factor. However, it is important to examine the evidence from failures to make sure that localized overheating or excessive voltage stress are not the main factors and corrosive sulfur a minor contributor.

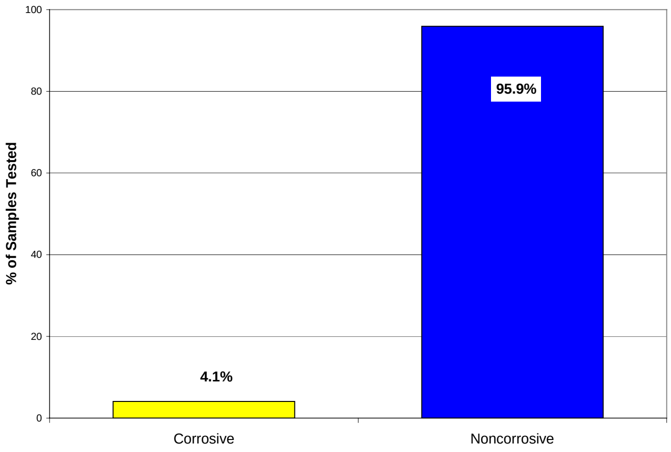
DETCTION OF THE PROBLEM – TEST METHODS FOR CORROSIVE SULFUR

Worldwide there are specifications for corrosive sulfur in electrical insulating mineral oils. This is because mineral oils contain corrosive sulfur compounds that must be removed to a high degree in the refining process for manufacture of electrical insulating oils. The effectiveness of the removal of corrosive sulfur compounds should be verified and hence is specified. The corrosive sulfur problem is of sufficient magnitude that it cannot be treated as an unusual occurrence. Standards organizations have revised or are in the process of revising present test methods and specifications for a more rigorous evaluation for corrosive sulfur.

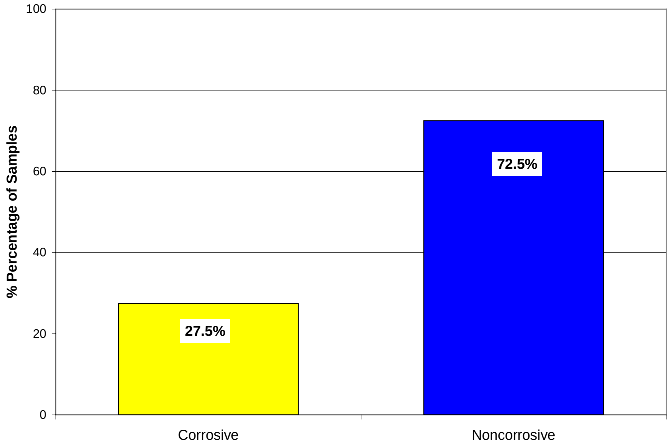
It is the authors' belief that more than one corrosive sulfur method is needed. We are recommending the use of a bare copper method, ASTM D 1275B, and a covered conductor test performed in two ways. In addition we recommend that the test be performed for dibenzyl disulfide to determine if it is in the oils being used on your system.

At Doble Engineering Company, we have revised our insulating mineral oil specification requirements for corrosive sulfur by modifying the ASTM method D 1275A, to an extended test now identified as ASTM D 1275B. Doble undertook the original research on this method in response to a few failures in the US due to corrosive sulfur. The oil involved either failed the D 1275A test or marginally passed it. At the time it could be seen that there was not enough margin in the corrosive sulfur test for the application. In subsequent testing to date, we have found that the oils from failed transformers with evidence of copper sulfide formation did not pass this modified test ASTM D 1275B, but did pass ASTM D 1275A. FIGURES 7 and 8 show the difference in populations of oils that are determined to be corrosive and non-corrosive by the old (D 1275A) and the modified method (D 1275B). As shown in the FIGURES 7 and 8, the modified method is a much more rigorous test. The D 1275B test is performed with a bare copper strip at an elevated temperature of 150°C for an extended period of time of 48 hours.

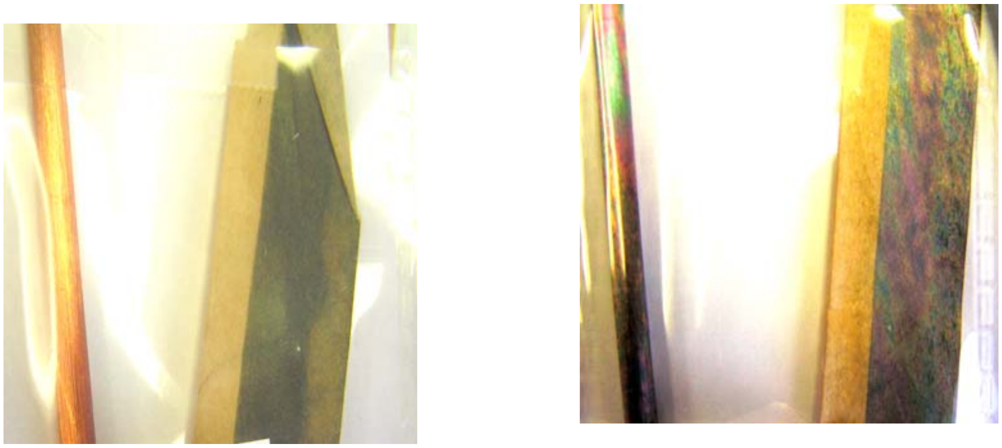
In addition to the bare copper test it is important to have a measure of the propensity to form copper sulfide deposits in the paper insulation. For this a covered conductor deposition (CCD) test is used. This test was first described by ABB [3] and has since been used in various forms by other researchers. Doble recommends that the test be performed with both sealed and breathing tubes as oils vary in their deposition behavior as influenced by the amount of oxygen available. This is very important, as we have found some oils will pass the sealed tube test and fail the breathing tube test. It is extremely important to characterize the deposits, as some appear to be relatively benign aging byproducts, while others are copper and copper sulfide deposits. Differences in deposits can be seen from FIGURE 9.



Percent of Oils that Fail ASTM D 1275A
FIGURE 7

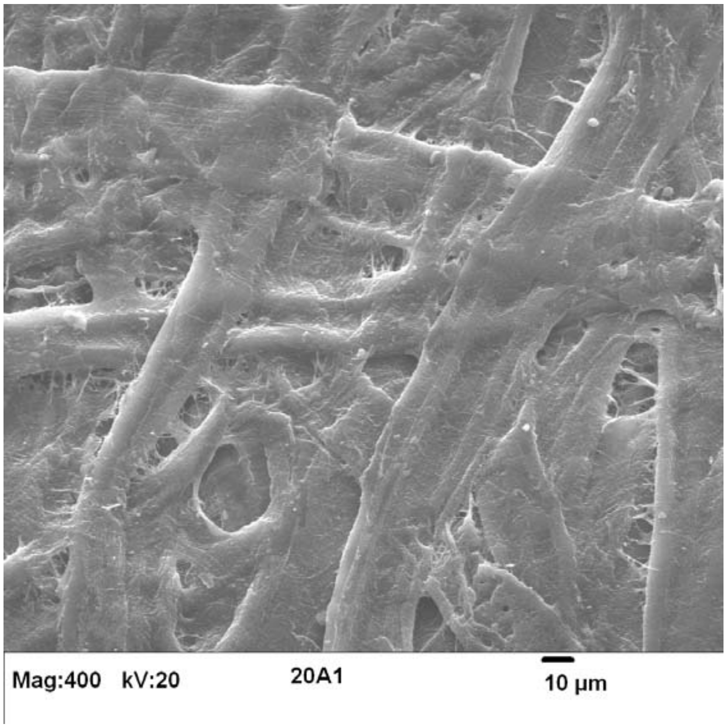


Percent of Oils that Fail ASTM Test D 1275B
FIGURE 8

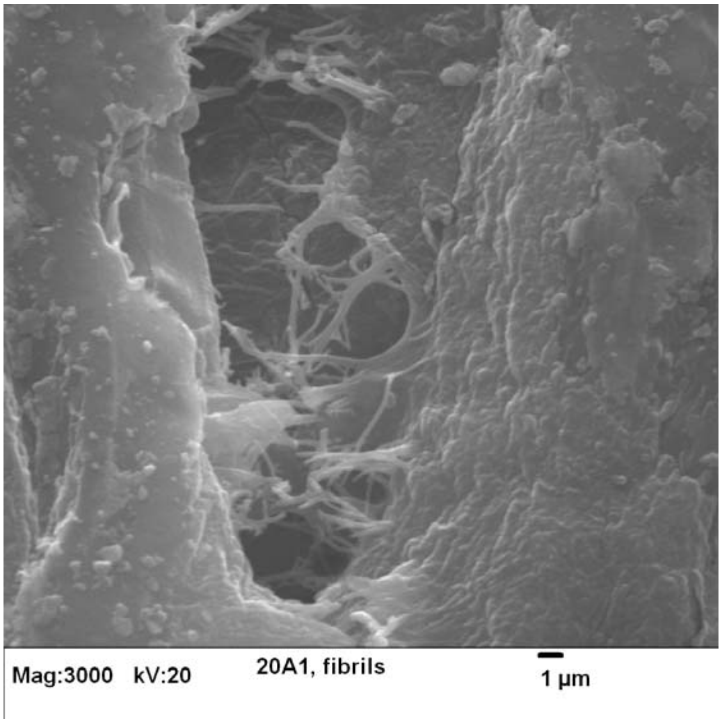


Deposits of Varying Composition on Paper from CCD Test
FIGURE 9

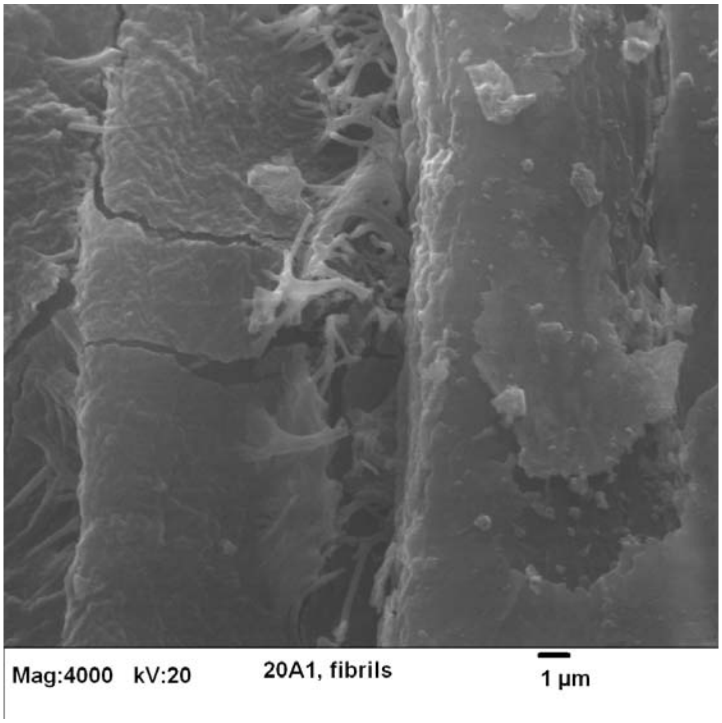
Doble has employed both dielectric breakdown voltage tests and scanning electron microscopy with an energy dispersive x-ray probe to develop an understanding of their effects on electrical properties and their elemental composition. FIGURE 10A-D and TABLE 1 respectively, show a SEM view and EDX analysis of deposits formed in the CCD test. In FIGURES 10A-D views are shown of two copper sulfide deposits at different magnifications ranging from 400 to 8000 times. At 400 times magnification shown in FIGURE 10A the coating on the fibers can be seen with some thin bridges of copper sulfide apparent. In FIGURE 10B the copper sulfide can be seen growing bridges between two fibers. Cracks in the copper sulfide coating can be observed on one of the fibers in FIGURE 10C along with the growth of bridges between fibers. FIGURE 10D provides the most highly magnified view where the new growth of the copper sulfide is clearly evident. We believe that the copper sulfide begins as small deposits on and perhaps in the paper then grows outward from the nucleus. The composition of the deposits and paper surface given in TABLE 1 shows the nature of one of the deposits and the relative amount of surface that it covers. The carbon and oxygen come from the paper fibers whereas the copper and sulfur are from the deposits. The results are clear evidence of copper sulfide formation with a high degree of deposition.



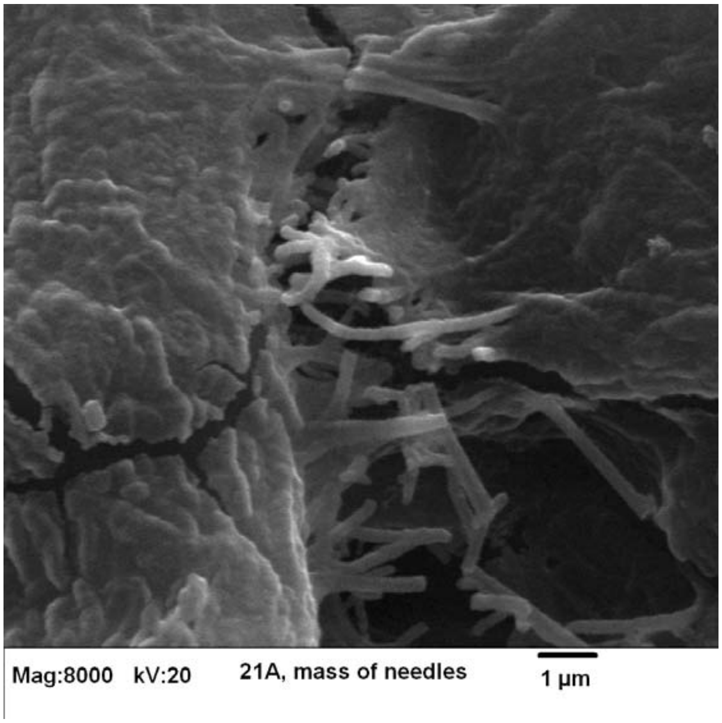
Copper Sulfide on Kraft Paper at 400 Times Magnification
FIGURE 10A



Copper Sulfide on Kraft Paper at 3000 Times Magnification
FIGURE 10B



Copper Sulfide on Kraft Paper at 4000 Times Magnification
FIGURE 10C



Copper Sulfide on Kraft Paper at 8000 Times Magnification
FIGURE 10D

TABLE 1
Composition of One Deposit

Element	Weight Percent
Elemental analysis of deposit only	
Copper	81.6
Sulfur	17.1
Calcium	1.4
Elemental analysis of wide area	
Oxygen	32.3
Carbon	16.1
Copper	40.1
Sulfur	6.9
Calcium	0.6

One compound has been identified as a potential corrosive sulfur agent, dibenzyl disulfide. The exact mechanism is not clear, but when spiked in an oil with almost no detectable sulfur, it has been shown that the by-products of this compound will indeed attack the copper. Sulfide deposits are formed on the copper, and copper and sulfide deposits on the paper insulation. One of these by-product compounds is benzyl mercaptan. The byproducts are formed at the elevated temperatures in corrosive sulfur tests such as 140 and 150°C and likely at lower temperatures seen in operating transformers. In a high oxygen environment, the mercaptan byproduct reforms (2 molecules join) into dibenzyl disulfide (DBDS). This might be one of the reasons that DBDS appears to have been more of a problem in sealed transformers. Although, we believe that dibenzyl disulfide might have been a contributor in some failures involving corrosive sulfur, it is not the sole reason for corrosive sulfur failures. How much of a contribution the dibenzyl disulfide makes needs further research.

Doble concludes that testing for corrosive sulfur should entail all three tests: ASTM D 1275B for bare copper effects, CCD for propensity to form deposits in paper (with sealed and air breathing tubes), and DBDS a compound that we would consider a potential contributor to corrosive sulfur failures. The test for DBDS need not be for every sample but should be to determine if this is in the oils used in your system. As additional research is performed, it is possible that new test methods will be developed. However, to help prevent this problem from becoming widespread, we would recommend the use of these existing methods.

Corrosive sulfur is not unique to transformer mineral oils. Materials used in electric apparatus or to fill electric apparatus with oil may contain sulfur compounds, some of which may be corrosive. This includes hoses, gaskets, some water-based glues, copper, and paper insulation. Care is required in selection of materials for compatibility with mineral oils. Materials in contact with the oil should not add corrosive sulfur in amounts that would make the oil "corrosive" as measured by appropriate tests.

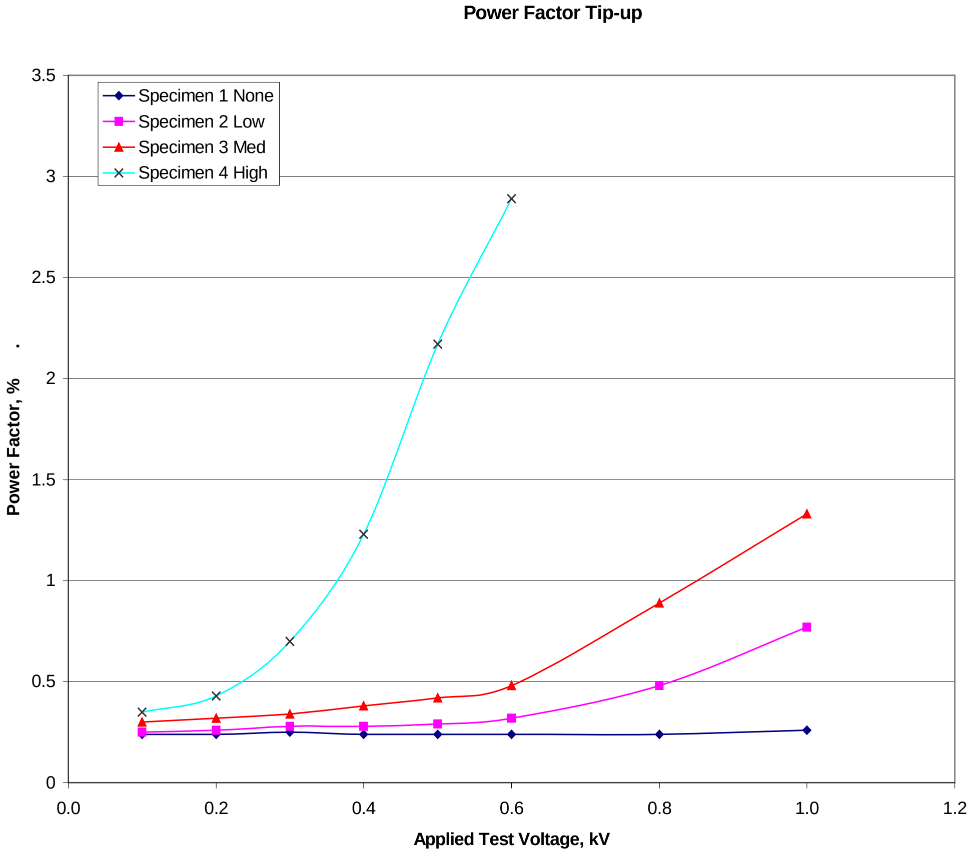
DETECTION OF EXISTING PROBLEMS

To date failures have occurred without prior evidence of an incipient fault. This makes the problem difficult to detect and manage. The failures have generally occurred after several years of apparatus being in service. The corrosion process appears to take this time to form critical amounts of conductive sulfides.

Dissolved gas-in-oil tests are routinely used to detect developing problems from overheating, partial discharge activity, or arcing. To date there has not been any indication of partial discharge activity or arcing in these units using dissolved gas-in-oil analysis, even when a sample was taken one day before the failure and in another case one week before the failure.

The best indicator of copper sulfide in the solid insulation has been power factor testing. Power factor tip-up, the change in power factor with applied voltage appears to be a distinctive characteristic to certain types of uncommon contamination/deposition such as that from conductive copper sulfide deposits. Normally, oil-paper insulation systems do not exhibit power factor tip-up. Power factor tip-up results from laboratory tests on paper purposely contaminated with purchased copper sulfide are shown in FIGURE 11. The dry oil-impregnated Kraft paper specimens where contaminated with different visible amounts of copper sulfide on the surface and the power factor was then measured. The relative amounts of copper sulfide were given as none, low, medium and high. The results show that the power factor and the tip-up increases with increasing degree of contamination.

To date the best means found for detecting corrosive sulfur in transformers and reactors has been the measurement of the power factor of the main apparatus insulation at high voltages. With high voltage apparatus, insulation power factor tests of the main insulation have been performed up to 35 kV. Tip-up has been detected with some units that have had oils that failed the ASTM D1275B test. The units tested had other characteristics of transformers at risk for corrosive sulfur deposition.



Power Factor Tip-up of Laboratory-Prepared Oil-Impregnated Kraft Paper
FIGURE 11

To date the main means for detecting corrosive sulfur problems have been by internal investigation. Testing of the oil can determine if the apparatus could develop a problem, but it is the internal inspection that has revealed the evidence of copper sulfide formation. Often the most visible evidence is on copper surfaces. If there is exposed copper, the tarnish will sometimes be visible especially in areas where there are connections. As the tarnish gets worse it turns gray and can be mistaken for carbon from overheating or a failure. Unwrapping the copper conductor can reveal further tarnish. The amount of corrosion is not uniform in a disk (as can be seen in FIGURE 1), or throughout the windings.

It is the deposition in the paper that is really the key to determining the risk of failure from corrosive sulfur. In some cases the copper sulfide can be visibly seen on the paper insulation and ranges considerably in coloration depending upon severity, oxygen levels, closeness to the conductor, and other factors. Copper sulfide is also not uniformly distributed in the paper insulation and it is important to search for it all around a failed area and in multiple suspect regions. However, this is not a task performed on a transformer that would be have continued service as it would require dismantling of the unit.

INTERIM METHODS OF MITIGATION

It is likely that there is a substantial amount of oil in service in large power transformers that can cause the sulfur corrosion problems. Although these oils with excessive amounts of corrosive sulfur represent a very small percentage of the total oil volume in service, they are important as copper corrosion and sulfide formation cannot be reversed. Once a corrosive sulfur problem is detected, it might be possible to mitigate against further significant corrosion. Possible methods include removal of the corrosive sulfur compounds, oil replacement, partial oil replacement, and passivation using metal deactivators [4]. Means for removing corrosive sulfur compounds from the oil have been studied and require further investigation. Depending on the size of the problem this may be an area for future research. Preliminary studies at the Doble Laboratories have shown that mineral oils can have considerable differences in the temperatures they will begin to form copper sulfide under test conditions. Mixing of higher corrosive sulfur content oils with those with very low sulfur contents can significantly improve the formers characteristics well beyond acceptable limits as seen in TABLE 2. Further study is being performed to examine the deposition characteristics of mixtures of oils. ABB has shown limited data at the 2006 Doble Life of a Transformer seminar that mixtures might not be effective in retarding deposition effects.

TABLE 2
Corrosive Sulfur Properties of Mixtures of Oils – Bare Copper Tests

Oil Combinations	150°C 48 hrs	150°C, 48 hrs 160°C, 24 hrs	150°C, 48 hrs 160°C, 24 hrs 170°C, 24 hrs	150°C, 48 hrs 160°C, 24 hrs 170°C, 24 hrs 180°C, 24 hrs
100% Corrosive Oil	**CORROSIVE**			
100% Non-corrosive oil	Non-corrosive	Non-corrosive	Non-corrosive	Non-corrosive
50% Corrosive Oil **50% Non-corrosive Oil**	Non-corrosive	Non-corrosive	Non-corrosive	**CORROSIVE**
25% Corrosive Oil **75% Non-corrosive Oil**	Non-corrosive	Non-corrosive	Non-corrosive	**CORROSIVE**
10% Corrosive Oil **90% Non-corrosive Oil**	Non-corrosive	Non-corrosive	Non-corrosive	Non-corrosive

Another method that has been employed is the use of a passivator that binds up some of the active sites on the metal surface retarding reactions with corrosive sulfur. The passivator also retards the deposition mechanism for copper and copper sulfide in paper as seen by CCD tests. Some experiments with passivators have shown that in some cases there is some stray gassing behavior – the thermal decomposition that creates combustible gases (often mostly hydrogen) and carbon dioxide. The stray gassing seems to be base-oil dependent and might be a short-term phenomenon. The passivator can also eventually form a sludge-like material similar to that formed by the oil. This passivator oxidation by-product would not appear to be any more adverse than that from the oil except that in some laboratory tests the passivator byproducts tended to remain suspended in the oil instead of settling out and adversely affect the dielectric strength of the oil. More research is needed to better understand how well these methods will work and the long-term benefits. For the immediate future these methods appear to be promising and could help mitigate developing problems. Some companies have already started using these approaches.

CONCLUSIONS

Recently the electric power industry has seen an old problem resurface, corrosive sulfur in oil. Enough problems have occurred around the world that the industry needs to respond and is doing so. This includes changing specifications, identifying where problems could exist with appropriate tests, and developing methods for mitigation. Doble Engineering Company has already changed its transformer oil purchase specification and is undertaking a collaborative study with industry participants to help solve this problem. International standards organizations have already started the process to modify existing methods and/or develop new ones. With a quick response this problem can be managed to minimize its' impact on the industry. It is unlikely that one single test will provide the solution to identifying the corrosive sulfur issues in a transformer or reactor. It is likely however, that several tests in combination will provide the information necessary to make the appropriate assessments concerning the condition of electric apparatus and components.

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AUTHOR BIOGRAPHIES

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Mr. Griffin has been with Doble since 1978 and held the position of Laboratory Manager before becoming Vice President of Laboratory Services. Since joining Doble, Mr. Griffin has published over 50 technical papers pertaining to testing of electrical insulating materials and laboratory diagnostics. He is a Fellow of ASTM and a member of Committee D-27 on Electrical Insulating Liquids and Gases. He was formerly ASTM Subcommittee Chairman on Physical Test, ASTM Section Chairman on Gases in Oil, and the Technical Advisor to the U.S. National Committee for participation in the International Electrotechnical Commission, Technical Committee 10, Fluids for Electrotechnical Applications. Mr. Griffin is a member of the IEEE Insulating Fluid Subcommittee of the Transformer Committee, and the American Chemical Society.

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