



Addendum A

Doble Collaborative Study

Corrosive Sulfur Problems in Electric Apparatus: Causes, Prevention, and Mitigation

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Proposal by: Paul Griffin and Lance Lewand
Doble Engineering Company
85 Walnut Street
Watertown, MA 02472



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Executive Summary

Introduction

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 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. ASTM, Doble Engineering Company, the International Electrotechnical Commission, and other specifications require that the oil be non-corrosive in accordance with a specific test method. Recently there have been a number of failures of power transformers and reactors where there are indicators of copper corrosion and formation of conductive copper sulfides on conductors and insulating materials. The conductive copper sulfides likely reduce the partial discharge inception voltage and more importantly reduce the dielectric breakdown voltage of the solid insulation, which can result in a dielectric puncture through the paper insulation. The failures have occurred after the apparatus have been in service for some years. At operating temperatures the corrosion process appears to take this time to form critical amounts of conductive sulfides. To date the failures have occurred without prior evidence of an incipient fault and therefore it appears that this problem is difficult to detect and manage. At least some of the oils in these failures met the requirements of ASTM D 3487, IEC 60296, and the Doble Transformers Oil Purchase Specification (TOPS), probably as new and after being in service.

Corrosive sulfur problems were found early in the first half of the twentieth century. As early as 1948, F. M. Clark and E. L. Raab issued a report to ASTM Committee D-27 on the subject of method development to detect corrosive sulfur. This research eventually led to the creation of ASTM Method D 1275. Of interest is that they developed this new test method, as the one in use, ASTM D117, was found to be inadequate. One possible explanation was that transformers were operating at higher temperatures and so a higher temperature test was required. It was recognized that the oil could have benign sulfur compounds that became corrosive at elevated temperatures. ASTM D 117 was developed to detect free sulfur and corrosive sulfur compounds already present in the oil. It is apparent that the present ASTM test method was developed, such that sulfur corrosion would not be expected to occur in electric apparatus even from conversion of sulfur compounds from non-corrosive to corrosive. It would also appear that the method was developed so the test could be completed in a reasonable amount of time. We now know that even the present methods for corrosive sulfur detection, ASTM D 1275 and DIN 51353, are inadequate.

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 which would include not adding corrosive sulfur to the mineral oil in amounts that would make the oil "corrosive" as measured by appropriate tests. It may be that more education and care is required in the industry, along with appropriate testing to make sure that materials are adequate for the application. Many of the problems that have occurred recently have not been associated with material compatibility problems with the oil.



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It is clear that the present specifications must be improved and that a better understanding of the mechanism of sulfur corrosion is needed. It is likely that there is a substantial amount of oil in service in large power transformers that can cause the sulfur corrosion problems that have been associated with recent failures. Although copper corrosion cannot be reversed, it is possible to mitigate against further significant corrosion. Possible methods include oil replacement, partial oil replacement, and passivation using metal deactivators.

Transformers have been around for over 100 years and yet much remains unknown about the complex insulation system. Even a single component, the transformer oil, is a complex mixture of molecules which are not completely identified. For this reason, the simplest recourse for solving problems with insulation systems is to determine limitations through experimentation. If a complete analysis is possible, so much the better for prevention of future problems.

Doble Engineering company has issued this proposal to provide the information to better understand, prevent and mitigate sulfur corrosion in power apparatus. By performing the research collaboratively we can make greater strides in solving this problem before more apparatus are put at risk. The risks are real and there is a growing pool of evidence that the failure rate from sulfur corrosion problems is growing and measures need to be taken now to prevent starting new problems and to identify and mitigate "at risk" units now in service.

One of the goals of the study is to gain acceptance of the need for change with the evidence that a study of this magnitude can bring. To date we have had refiners, manufacturers, utilities, research organizations, and insurers express interest in collaborating and together we will help make the changes that are needed for the industry.

To facilitate the exchange of information all of the participants in the study will be listed along with their contact information. We ask that this information be used only for the collaborative effort and only with participants. If any of the participants would not like their contact information listed, this of course would be respected.

Major Elements of the Proposal

1. Time and temperature dependence of sulfur corrosion

Transformers are designed to operate at specified temperatures. It is desirable that significant sulfur corrosion will not occur during the life of the electric apparatus which can be for many decades depending on the operating temperature, maintenance, and other factors. The time and temperature dependence of sulfur corrosion will be examined with oil and copper systems, and also with oil, copper, and paper insulation systems. As the project would become too extensive to test all oils to the same degree there will be an initial set of tests to determine some basic temperature dependence for formation of copper sulfides. A wide range of refiners electrical insulating mineral oils will be tested over a short period of time to determine their propensity for corrosive sulfur reactions with copper and



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silver. This will include oils from those that have not joined the collaborative study and may include oils that are no longer commercially available. The test protocol is as follows:

Temperature, °C	Time, hours	Copper	Silver	Paper wrapped
140	19	x	x	Yes/No
140	48	x	x	Yes/No
150	48	x	x	Yes/No
175	24	x	x	Yes/No
200	24	x	No	No
225	24	x	No	No

Note the two tests at 140°C will be performed independently. Starting at 150°C the test will be performed sequentially using a single sample. For example the sample tested at 225°C will have been subjected to 48 hours of heating at 150°C, and 24 hours each at 175 and 200°C before heating at 225°C. This will allow us to separate the oils for further testing into groups varying in the temperature at which sulfur corrosion is evident. Preliminary work has shown that there is a significant difference in the sulfur corrosion characteristics of mineral oil products. Temperatures as high as 225°C are used to quickly reveal differences in oils. Tests will be performed in glass vessels with o-ring seals. Samples will be purged with nitrogen to remove most of the oxygen present from air as presently called out in ASTM D 1275. Increased times for nitrogen purging will also be examined and tests performed on the oil to verify the oxygen content is sufficiently reduced.

Oils for this study can be provided by participating refiners and others. As many commercial products as possible will be evaluated. Refiners can also include possible new products under development. A list of all of the products in the study will be listed but individual products will not be identified except to those providing the oils. There is a wide difference in the performance of oils for this testing. As refiners may make changes in their products from time to time, and these tests are very simple to reproduce, the identification of individual products with the results is not required. The goal of the study is to provide a better understanding of the phenomenon, to develop better tests methods to detect potential problems for prevention, and to enhance our knowledge on mitigation. The information linking the refiners and the results for this part of the study would not be published without written permission from the refiners or suppliers of the oils.

The results of this part of the study will be used to determine which oils will be used in the more extensive testing given in subsequent items, including more information on time and temperature dependence of the copper sulfide formation.

2. Aging materials and conditions

A large part of the project will be to study oils under a variety of accelerated aging conditions to reveal real differences in corrosion characteristics. We will attempt to identify the variables that exacerbate formation of copper sulfides on conductors and in the paper insulation. For these tests both clear bottles with o-ring seals and sealed steel aging tubes will be used depending on the extent of aging and the tests to be performed. See attached spreadsheet for the testing matrix. Note that the analytical tests



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to be performed on the oil, paper, and copper will occur at different times depending on type of aging, temperature, analytical test and test results. Some of the aging will be completed at a set time (such as aging of paper), while other aging tests will be terminated when corrosion occurs. Some of the aging tests will be run in duplicate and some will have sacrificial samples for time dependent study.

Copper – Both new and corroded copper will be used to provide an understanding of issues for new equipment, and for apparatus that have been in service with oils that are more disposed to formation of metallic sulfides. Preliminary studies suggest there are some differences in the performance of new and corroded copper.

Paper – Corrosive sulfur problems have occurred in transformers with thermally upgraded Kraft paper and with Kraft paper insulation systems. It is not known if thermally upgraded Kraft paper with dicyandiamide and other nitrogen containing compounds retards sulfur corrosion. It is also not known if the different paper materials behave the same in terms of copper migration, particularly in a corrosive environment. In addition to corrosion issues, paper life assessment will be examined as measured by change in degree of polymerization and using standard guidelines for life estimation. Some of the thermal upgrading agents will be added to oil directly to determine the effect on retarding copper sulfide formation.

Oils – Doble has performed preliminary experiments and found that some transformer oils have sulfur compounds that are corrosive or become corrosive at temperatures between 150 – 170°C. In these same experiments other oils did not significantly tarnish copper strips even at temperatures as high as 250°C. Based on the results of studies in item 1 (Time and temperature dependence of sulfur corrosion) selected oils will be subjected to further testing. In addition, mixtures of oils that produce copper sulfides at lower temperatures, with those that produce copper sulfides only at very high temperatures or not at all will be studied. One means for selecting oils will be to use a Doble modified ASTM D 1275 method to be performed at 150°C for 48 hours (which is included in the Item 1 study). Oils that do not meet this requirement but pass the present ASTM D 1275 would be used in this study. Depending on the outcome of the other tests for time and temperature dependence of sulfur corrosion other oils will be selected. These studies will provide the basic information on differences in sulfur corrosion between oils and a better understanding of the ability to dilute corrosive sulfur species to acceptable concentrations with commercially available products.

Antioxidant and Oxygen – Competing reactions occur in the insulation system of electric apparatus. Oil and copper oxidation appears to compete or interfere with formation of copper sulfide. These reactions will be studied to better understand their influences. An approved anti-oxidant will be added to an uninhibited oil to study the effects of inhibitor. Short-term and long-term differences may occur with systems that have some consistent ingress of oxygen such as a free-breathing conservator system in comparison to a sealed membrane or nitrogen-blanketed system. To study this a controlled leak will be used to see the effects of oxygen ingress on copper sulfide formation and deposition.

Analytical tests that will be employed for the aging studies include:



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Paper: visual examination of metal strips and paper, copper or silver content, sulfur content, water content, dielectric breakdown voltage, degree of polymerization of paper (DP), and power factor or dissipation factor at multiple voltage stresses and frequencies.

Oil: interfacial tension, acidity, dielectric breakdown voltage, power factor or dissipation factor, water content copper or silver content, passivator content, sulfur speciation for specific compounds, and corrosive sulfur.

3. Voltage and Current

Electric fields may influence formation and deposition of metallic sulfides. Tests will be performed to examine the contribution of electric fields on sulfur corrosion and deposition.

To study the effects of voltage on copper corrosion and copper sulfide deposition a sealed system will be used with paper wrapped and exposed copper electrodes using a voltage stress of 100volts/0.001 inches of insulation. This will be done at the same temperature as a control which will be an identical setup without an applied voltage.

Effects of current on copper sulfide formation and deposition will be examined using a sealed system with paper wrapped and exposed copper electrodes using a current flow of 2800 amps. This will be done at the same temperature as a control which will be an identical setup without applied voltage and current flow.

4. Metal Sulfide Deposition on Paper Insulation and Copper Migration in Insulation Systems

ABB published a paper at the 2005 Doble Conference showing that the deposition of copper sulfide on paper insulation can occur, but the phenomena is not fully understood by extrapolation from metal strip-sulfur behavior. The conditions and competing reactions of sulfide formation on metal surfaces and deposition on paper insulation structures will be investigated to provide a better understanding of the conditions that promote deposition on insulation and the differences between electrical insulating oils. Samples with oil and paper will be aged at several temperatures ranging from 110 to 170°C.

5. Prevention

One of the goals of the study is to have a better specification for electrical insulating mineral oils as a preventive measure. Doble intends to change its specification in 2006. Other organizations will need knowledgeable people to promote and educate others on the need for changes in the oil specification. This study is intended to provide necessary information for such change.

6. Mitigation

There are some transformers and reactors in service that contain oils that might cause sulfur corrosion to such a degree that premature failure may occur. There are several ways that it may be possible to substantially retard further corrosion and metal sulfide deposition. These include oil replacement,



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partial oil replacement, and passivation. An extensive study will be performed on the use of passivators as this is the least costly alternative, but as with any additive, difficult to predict in-service performance. Studies will be performed to simulate field experience by first aging samples with oils that do not pass the Doble modified corrosive sulfur test and then taking remedial steps at times that correlate with several years of service experience. Passivated oils will be tested for typical properties in addition to mitigation of corrosive sulfur reactions to retard formation of conductive sulfides on metal surfaces and in the cellulosic insulation. The effects of passivator on “stay gassing” (gassing at modest operating temperatures) and gassing under partial discharge conditions will be examined. The effects of passivator on the dissipation factor and dielectric breakdown voltage of the cellulosic insulation at power frequency and lightning impulse conditions will be examined.

7. Identification of Corrosive Sulfur Compounds

An effort will be made to identify corrosive sulfur compounds in new and aged oils. Several methods will be employed including gas chromatography, mass spectroscopy, and a general test for mercaptans. Tests will be made to detect intermediate compounds such as free sulfur and mercaptans that could be formed at elevated operating temperatures. This will not be an extensive study, as it would be easy to lose too much resource doing this without benefit.

8. Effects on Contact Resistance

One of the deleterious effects of metal sulfides is to increase the resistance of contacts. This ultimately will result in overheating and in the most severe cases thermal runaway of the contacts and failure. The investigation will determine the effects of metal sulfide films on resistance. This will not be actual contact tests but an examination of the effects of copper sulfide on surface resistivity of copper and silver strips.

9. Field Tests to Detect Copper Sulfide Deposition in the Solid Insulation

In cases where sulfur corrosion of an in-service transformer is suspected it would be extremely useful to know the degree of copper sulfide deposition in the windings and other solid insulation. A combination of controlled laboratory experiments and field tests (as possible opportunities arise) will be performed to determine which test methods best detect this problem.

10. Dielectric Breakdown Strength of Copper Sulfide Contaminated Insulation

Paper insulation will be aged with oil that deposits copper sulfides. The dielectric breakdown voltage of the paper insulation will be measured at various times as copper sulfide deposition increases to determine resistance to breakdown at power frequencies and under lightning impulse conditions. A control oil that does not form copper sulfide deposits will be tested under the same conditions. As corrosive sulfur may also effect copper migration in paper this aspect will also be examined.

11. Case Studies



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Information will be collected on field problems involving corrosion from sulfur compounds to determine patterns that may provide insight into the mechanism(s) of corrosion and conditions that result in failures. As much detail as possible will be included. If information from teardowns are available this will also be incorporated into the report. As it is critical to have a compilation of all the information from failures we would include nameplate information and the any oils that had been in the equipment, pictures, test results, reports etc.

Webinars (Web based seminars or meetings) and Other Meetings

As participants in this study are located worldwide we will be making all meetings available by webinar. The way a Webinar works is that a moderator (Doble) runs the session. The moderator controls the slides and makes the presentations in English. The moderator controls the slide presentation using his computer which is linked via the web to a webinar service provider. The sound is carried through the phone system either by phoning into the webinar service provider number. Those attending the webinar are at their computer so they can view the slides and e-mail questions to the group.

Your site for the webinar needs to have a computer link to the webinar service provider. A high speed internet connection is required for reasonable speed. Sound is through the phone system and it is best if you have a speaker phone. If there are a number of people from your company viewing and listening to the webinar a projector can be used from your computer to enhance viewing. We routinely use webinar services and they work quite well. All the participants in the webinar can hear each other or see questions that are asked electronically.

We also welcome any of the participants to meet with us in person to discuss the study and related topics.

Participation

Doble Engineering Company is offering participation in this study to accelerate investigation in a time critical matter and to allow for worldwide input on the subject. We strongly feel that research must be performed at an accelerated pace that is not consistent with technical committee standards organizations activities and individual efforts. Doble and others have reported some of the findings on corrosive sulfur problems at technical conferences and seminars. We feel that prevention and mitigation of corrosive sulfur problems need to be undertaken with as much understanding as possible to make the best decisions. The problem is happening now and the longer the wait on corrosive sulfur problems that are developing the greater the permanent deterioration of the insulation system.

We believe that international participation is a strong point for having a collaborative effort. Input from global participants will help achieve the peer review critical mass and ensure a very sound study, perform by an independent company.

We have had many companies respond to our initial invitation to participate in the study. We want to encourage active participation by all. We welcome your recommendations for what research needs to



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be done, best methods and procedures for performing evaluations, and other details to make this effort the most valuable it can be to you. Please let us know your suggestions for suggestions for logistics, communications between participants including Doble and other matters of interest to you.

Contact Information

Paul Griffin
Vice President of Laboratory Services
Doble Engineering Company
85 Walnut Street
Watertown, MA 02472
USA

Phone: 617-393-2902
Fax: 617-926-0528
e-mail: pgriffin@doble.com

We look forward to your participation, and we strongly welcome your thoughts on this emergent issue.

Regards,

Paul Griffin