UPDATE ON THE CORROSIVE SULFUR ISSUE IN OIL-FILLED ELECTRICAL EQUIPMENT

by

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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. This has occurred even though the oils, in most or all cases, passed internationally recognized industry specifications including the corrosive sulfur test oil having passed the standard test (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]. 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. Although the number of failures has been small, (>30), the assets lost have been substantial. Examples have included the failure of a 500 kV shunt reactor and a 450 MVA autotransformer. 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.

EVIDENCE OF COPPER SULFIDE, PURPLE, GREEN, BLUE AND GREY DISCOLORATION OF CONDUCTOR FROM TRANSFORMER WITH FOUR YEARS OF SERVICE
FIGURE 1

EVIDENCE OF DISCHARGE ACTIVITY ON A DISK FROM A FAILED TRANSFORMER
FIGURE 2

APPARTUS AT RISK

The problem with corrosive sulfur is 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 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. 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.

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. Yet 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 the same type of phenomenon has occurred in other units that do not meet this criteria:

- Sealed units (gas blanketed, sealed conservators, etc.)
- Units that operate at higher sustained temperatures such as GSUs
- Oil that has the propensity to form corrosive sulfur compounds (do not mistake with oils that have a high sulfur content)
- Kraft paper insulated transformers (as opposed to varnished or enamel wired or thermally upgraded Kraft)

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 sulfide on the surface of the copper. As the sulfur builds up and layers, copper sulfide flakes start to fall off the surface and possibly into some 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 has gone beyond that point in which the 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.

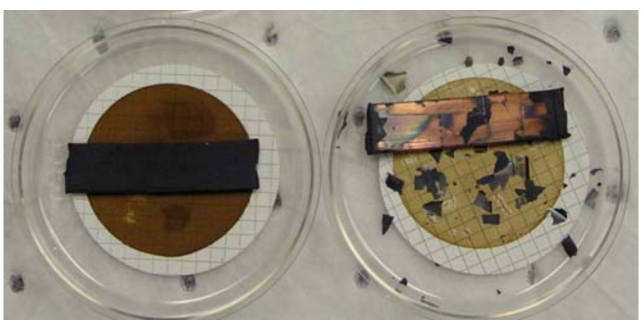


FIGURE 3

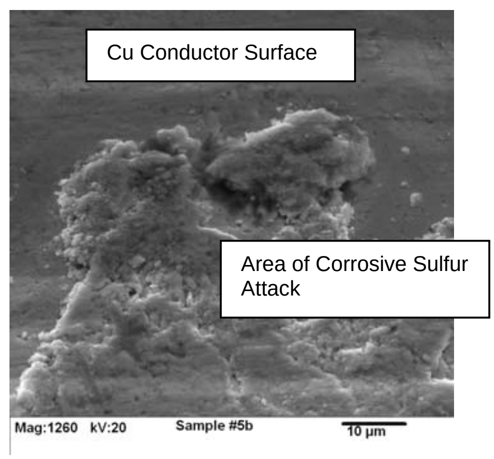


FIGURE 4

A closer look at the copper sulfide flakes (a conductive particle) actually shows copper sulfide crystals that form 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. 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).

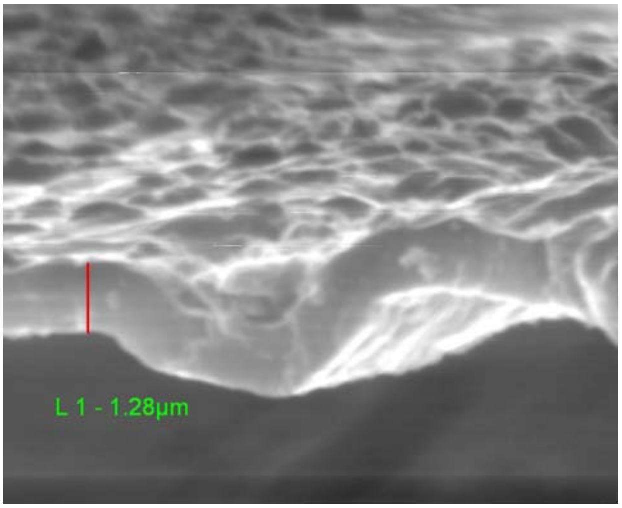


FIGURE 5

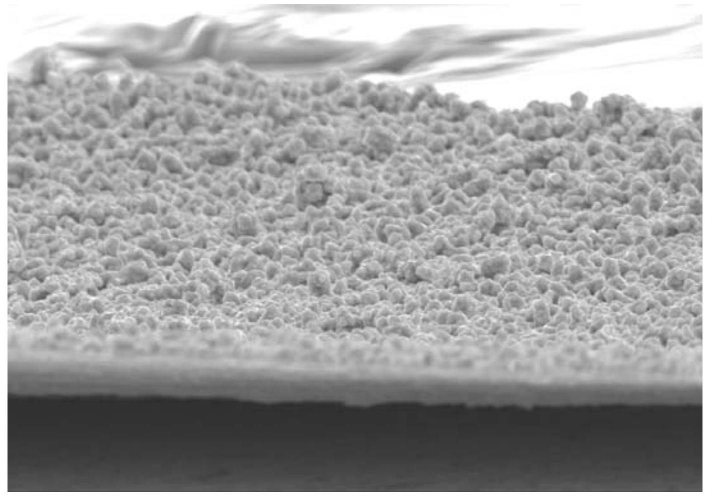


FIGURE 6

The second mechanism appears to be the cause 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 deposited on the paper or formed when copper ions migrate to the insulating paper and react with corrosive sulfur compounds to form copper sulfide deposits. It is also believed that some of the copper sulfide on the conductors is physically deposited by contact with the adjacent paper insulation. 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 (failure) (Figure 2) [2].

PRESENT RESEARCH WORK IN THE INDUSTRY

The corrosive sulfur problem has been a serious one for utilities, oil refiners and transformer manufacturers alike. There has been significant research performed by several entities over the past two years to identify, understand and most importantly determine methods to mitigate the problem. This is further demonstrated by the number of papers addressing this subject at this conference. Below is a brief synopsis of what has transpired during the past year:

ABB Studies	ABB has been extremely active in trying to understand the deposition of copper sulfide in the paper insulation and to develop a test to detect oils that form deposits in paper. The test is presently termed the CCD (Covered Conductor Deposition) Test [3]. A simplified form of this test and is presently undergoing a CIGRE round robin study involving 13 laboratories.
ASTM International	Committee D 27 undertook an emergency editing of the present ASTM D 1275 method. The new method was published in less than 3 months. It now contains two separate methods. D 1275A is the historic copper corrosion test performed at 140°C and 19 hours. D 1275B was derived from the Doble modified method which is performed at 150°C and 48 hours with several other changes. ASTM continues to look at other testing methods as well.
ASTM International	There are many analytical methods that ASTM has developed in other committees that may help in our application. Total sulfur content, ASTM D 2622; Sulfur speciation, ASTM D 5623; Copper Strip Tarnish Test, ASTM D 130; Inorganic chlorides and sulfates, ASTM D 878, and Mercaptans by potentiometric titration oil, ASTM D 3227 are just but a few that have been used in the present ongoing research by Doble and others
CIGRE	Working Group WG A2/32 is very active in corrosive sulfur and metal sulfide deposition research. They are presently conducting a round robin study of 3 different methods in which about 13 laboratories are participating including Doble. The testing program not only looks at copper corrosion but deposition in the paper as well.

CIGRE Brazil	Working group D1.01 have developed a copper corrosion test similar to that provided to ABINEE (a manufacturers' group) in Brazil by Doble. There are modifications that include testing the sample in triplicate with longer sparging times.
Doble Engineering	Doble has been actively performing corrosive sulfur research since 2001 and published a paper on the subject in 2002 [1]. At that time the modified corrosive sulfur tarnish method was developed and is now the basis of ASTM D 1275B. Lance Lewand is the technical writer for D 1275B for the ASTM subcommittee responsible for that method. Doble also instituted a collaborative research study which began in September, 2005 and now has about 30 members participating. Many of the world's refineries are part of the study along with utilities, an insurance company and transformer manufacturers. The study focuses on copper corrosion, copper sulfide deposition, copper and sulfur migration, the role of passivators, other mitigating procedures and transformer electrical tests used to identify a potentially identify a suspect transformer. Doble has also been involved in several failure analyses involving failed large GSU transformers.
IEC TC10	The International Electrotechnical Commission (IEC) Technical Committee (TC) 10 is examining methods to better evaluate corrosive sulfur in electrical insulating oils.
Oil Refiners	May refineries that produce transformer oil are performing their own in-house evaluations to make sure that the sulfur present in the oil does not become corrosive over time at elevated temperatures.
Siemens	Siemens is also extremely active in research and has provided the materials for the CIGRE round robin study and have developed their own method to check for copper corrosion by sulfur and possible copper sulfide deposition in the paper.

PREVENTION

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 are currently revising present specifications for a more rigorous evaluation for corrosive sulfur. At Doble Engineering Company, we have revised our insulating mineral oil specification requirements for corrosive sulfur by modifying the present ASTM method D 1275, now called ASTM D 1275B. In testing to date, we have found that the oils from failed transformers with evidence of copper sulfide formation did not pass this modified test, but did pass the present ASTM method. As additional research is performed it is likely that new test methods will be developed. However, to help prevent this problem from becoming widespread, immediate use of this more rigorous testing is recommended. Figures 7 and 8 shows 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).

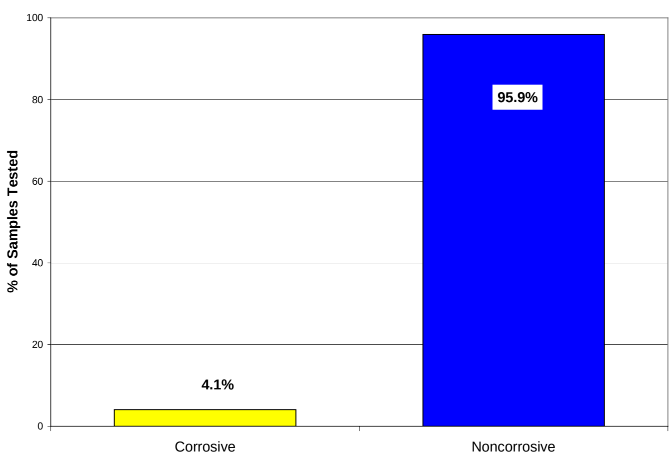


FIGURE 7

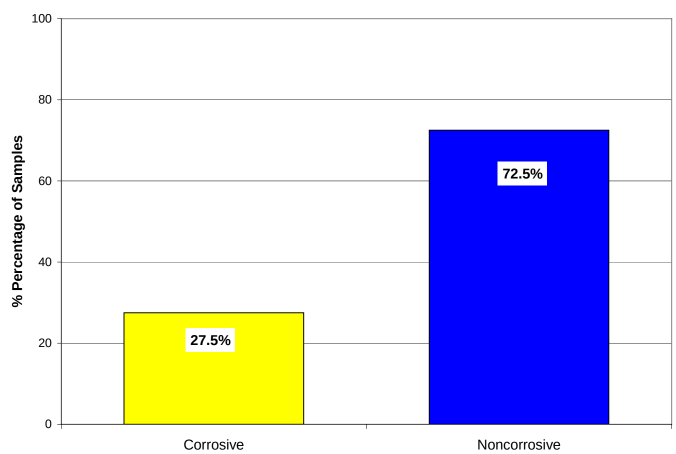


FIGURE 8

As shown in the Figures 7 and 8, the modified method, D 1275B, is a much more rigorous test.

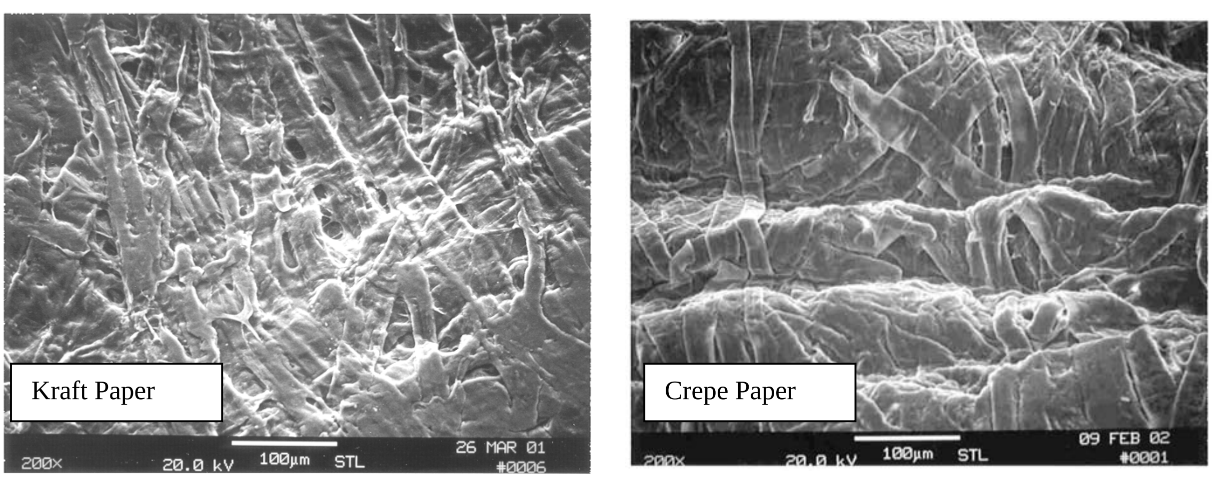
Corrosive sulfur is not unique to transformer mineral oils. Materials used in electric apparatus or to fill electric apparatus with oil may contain sulfur compounds, some of which may be corrosive. This includes hoses, gaskets, some water-based glues, copper, and paper insulation. Care is required in 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

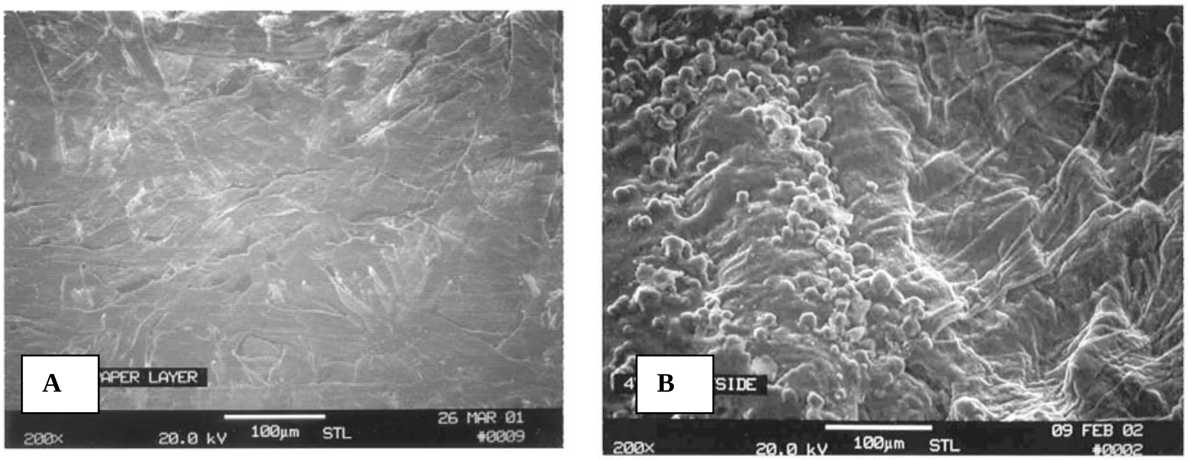
To date the failures have occurred without prior evidence of an incipient fault. This makes the problem difficult to detect and manage. The failures have occurred after several years of apparatus being in service. The corrosion process appears to take this time to form critical amounts of conductive 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. Although there can be an increase in the insulation power factor, this test has not been found to routinely detect this problem when performed in the standard fashion. Some laboratory investigations using power factor have been able to detect copper sulfide in paper under some conditions. More research is needed to determine if this can be applied to apparatus.

To date the best 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 be visible. 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.

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. Analysis of paper surfaces is shown in Figures 9 and 10 as performed by scanning electron microscopy (SEM) and energy dispersive x-ray (EDX) analysis. The SEM achieves high magnification and EDX is used to determine the elemental composition of any particles. Figure 9 shows normal paper, with the individual fibers clearly visible in both the Kraft and crepe papers and with no signs of foreign material present. Even the crimping of the crepe paper is clearly visible. When copper/sulfur or other metal/sulfur contamination of the paper surface occurs, the results can be profound as shown in Figure 10. It can be seen from the SEM photomicrographs at a 200 times magnification, that copper-sulfur contamination is clearly on the paper insulation. In Figure 10A all the fiber surfaces and the gaps between the fibers are encrusted with the metal sulfides. Figure 10B shows an earlier stage with what appears to be globs of metal sulfides and sulfates.



UNCONTAMINATED CONDUCTOR INSULATION
FIGURE 9



CONTAMINATED CONDUCTOR INSULATION
FIGURE 10

RESEARCH EFFORTS AND INTERIM SOLUTIONS

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, it is 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]. No simple means for removing corrosive sulfur compounds from the oil has been developed. 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 former's characteristics well beyond acceptable limits. 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. 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 testing and mitigation. Doble Engineering Company has already changed its 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 the transformer.

[1]. Lewand, Lance R., "The Role of Corrosive Sulfur in Transformers and Transformer Oil", *Proceedings of the Sixty-Ninth Annual International Conference of Doble Clients*, Boston, MA, Insulating Materials Session, 2002.

[2]. Lewand, L., "Investigating Copper Sulfide Contamination in a Failed Large GSU Transformer", *Proceedings of the Seventy-second Annual Doble Conference of Doble Clients*, Boston, MA, Insulating Materials Session, 2005.

[3]. Claiborne, C., Dahlund, M., Gustafsson, K, Hajek, J., and Hjortsberg, A., “Speficiation and Testing of Transformer Oils with Respect to Corrosion”, *Proceedings of the Seventy-second Annual Doble Conference of Doble Clients*, Boston, MA, Insulating Materials Session, 2005.

[4]. Lewand, R., “Passivators –What They Are and How they Work”, *NETA World*, Spring 2006.

AUTHOR BIOGRAPHIES

Lance Lewand

Lance Lewand is the Laboratory Manager for the Doble Materials Laboratory and is also the Product Manager for the Doble ***DOMINO®***, a moisture-in-oil sensor. The Materials Laboratory is responsible for routine and investigative analyses of liquid and solid dielectrics for electric apparatus. Since joining Doble in 1992, Mr. Lewand has published numerous technical papers pertaining to testing and sampling of electrical insulating materials and laboratory diagnostics. Mr. Lewand was formerly Manager of Transformer Fluid Test Laboratory and PCB and Oil Field Services at MET Electrical Testing Company in Baltimore, MD for seven years. His years of field service experience in this capacity provide a unique perspective, coupling laboratory analysis and field service work. Mr. Lewand received his bachelor of science degree from St. Mary's College of Maryland. He is actively involved in professional organizations such as ASTM D-27 since 1989 and is a sub-committee chair. He is also the secretary of the Doble Committee on Insulating Materials.

Paul J. Griffin

Mr. Griffin has been with Doble since 1979 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.