AN UPDATE ON UNDERSTANDING CORROSIVE SULFUR PROBLEMS IN ELECTRIC APPARATUS

Paul J. Griffin and Lance R. Lewand
Doble Engineering Company

ABSTRACT

Corrosive sulfur oil is known to have caused problems in electric apparatus and accessories. The problem is complex and continued research is necessary. However, some significant improvements in understanding have lead to better tools to detect possible problems and help avoid them. Two test methods for oils have been developed that are useful for detecting potential problem based on different failure modes. In-service oils can be tested and evaluated based on the application. Mitigation methods such as passivation are being evaluated.

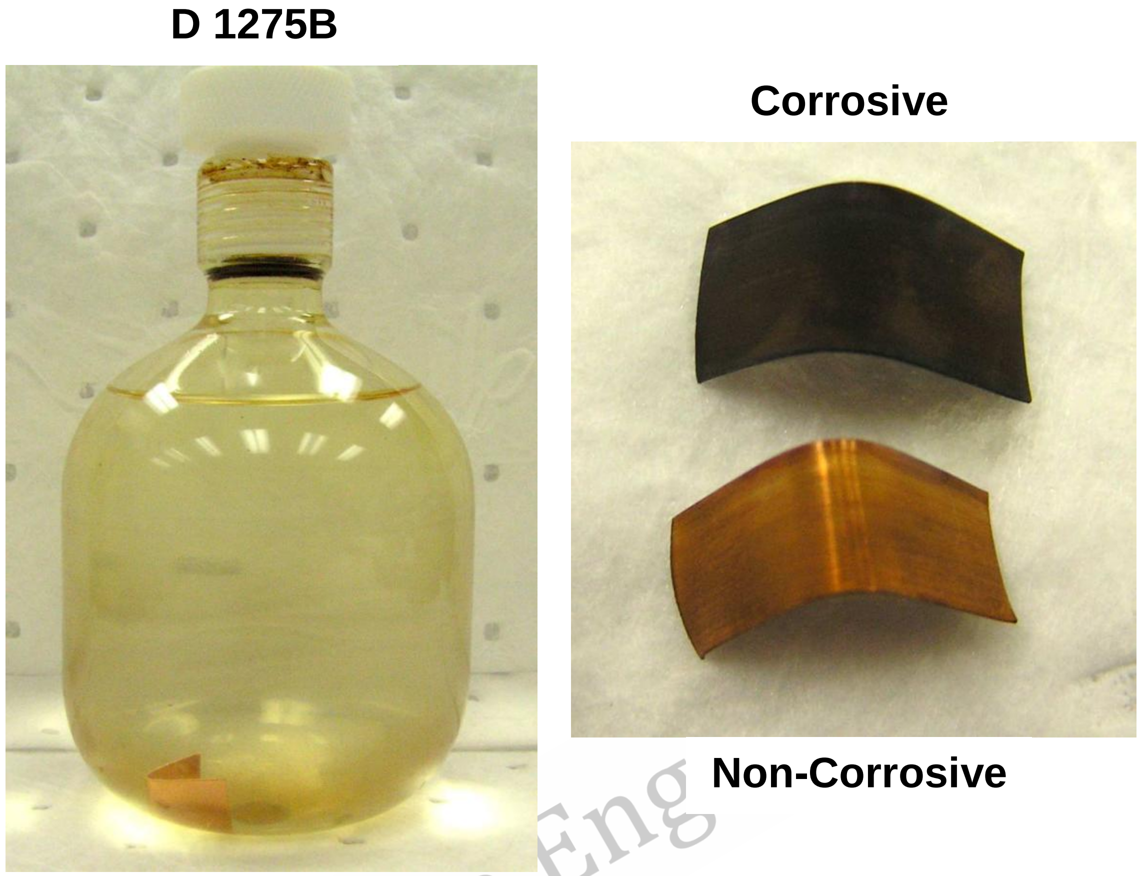
INTRODUCTION

There have been a number of problems and failures of power transformers, shunt reactors, load tap changers and bushings associated with corrosive sulfur in electrical insulating mineral oils. Although the number of failures continues to be a relatively small percentage of the installed base, the failures have been of some critical and costly assets. Problems have been reported in many countries worldwide. The extent of the problem has still not been determined, as test methods are just being developed to detect evolving problems for in service equipment. In many cases the cause of failure might not be correctly identified, as detecting corrosive sulfur problems is not easy in some cases. These corrosion problems tend to develop undetected in the apparatus over several years before failure occurs. This is a topic of considerable interest as seen by the number of recent presentations on this subject [1-19]

TEST METHODS TO DETECT CORROSIVE SULFUR IN OIL

Doble started investigating corrosive sulfur in transformer oils because of some failures in the 1990s. The problem was associated with an oil that was right at the edge of passing or failing the ASTM D1275 method. At that time ASTM D1275 was the only method under the jurisdiction of ASTM Committee D-27 on Electrical Insulating Liquids and Gases. The method, which eventually became ASTM D 1275A, involves a bare copper strip that is heated at 140°C for 19 hours under prescribed conditions. Studies by Doble examined a more stringent approach to this method, using a temperature of 150°C for 48 hours that increased the margins while allowing most oils to still meet specification. This modified method became part of the Doble Transformer Oil Purchase Specification in January of 2006 and was standardized by ASTM to be Method D 1275B later in that year. Figure 1 shows the set up and a pass and fail result for this test.

It is important that the test methods, as much as possible, detect aspects of oil quality that are functional in the application. For reactions that can take years to occur under operating conditions, some parameters are altered to accelerate the process for laboratory testing. These are often the most obvious factors that affect reaction rates, temperature, and in some cases oxygen content. However, these changes in conditions to cause acceleration of the reactions of interest can also introduce artifacts – things that are introduced by the experimental conditions that change the natural reactions. An example would be accelerated oxidation tests. It is well established that the gains seen by adding antioxidant to oils in the commonly used accelerated oxidation tests are not realized in service. Therefore it is helpful to establish as many links as possible from laboratory scale tests to in-service performance.



ASTM D 1275B
FIGURE 1

The failure modes that are most consistent with the D 1275B test are those that involve coating of conductors with a metal sulfide film. This film or coating is resistive compared to bare metal contacts and can result in their overheating. Another potential failure mechanism is the result of a thick coating of the copper sulfide flaking from the conductor into insulation structures. Figures 2a, b, and c show a few examples of the black metallic sulfide films on conductors. In the case of bushings the copper sulfide on the conductor is more of an indicator of the corrosion process rather that the failure mode. The failure mode was actually from discharge activity within the paper of the core. However, it does reveal the coating of the bare copper and the flaking phenomenon. The tap changer contacts were from a 34.5 kV, 7 MVA 1971 transformer with aluminum windings. The contacts were found to be coated with metal sulfide, which is resistive compared to the bare metal. This was the apparent cause of excessive gassing indicating localized high temperature overheating of the oil. These bare-metal reactions can occur even when reactive metals are in relatively small concentrations. This transformer had aluminum windings and the sulfide films were found on the contacts and some bare copper surfaces. The copper sulfide coated ring shown in Figure 3 is from a failed transformer [5].

Progress has been made in recent years. Some new (meaning unused) commercial oils from the late 1990s and early 2000s tested by the more rigorous D1275B requirements would not have passed. However, commercial oils tested in this same way in a recent study all passed when tested in accordance with ASTM D 1275B. This suggests that the refining industry has responded to this change in requirement for transformer oil. Most new and in-service oils tested over the past ten years would be expected to pass ASTM D 1275A and in our studies only 4% of oils did not pass this criterion. However, when the more rigorous D 1275B is used a much higher percentage of oils, about 28% fail the test. It is not expected that most of these oils will cause problems with electric apparatus, but their application should be examined carefully as will be discussed later in this paper.

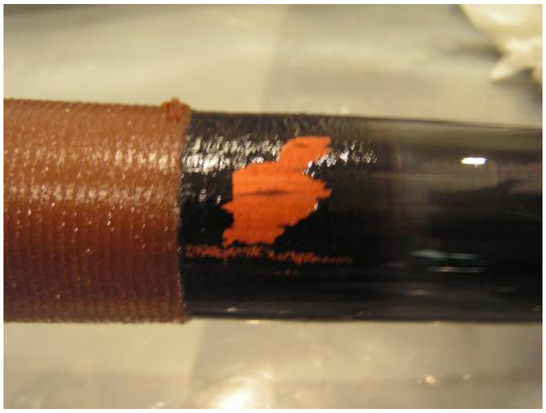


Figure 2a: Copper Sulfide on Bushing Center Conductor

Figure 2b: Sulfide Deposit on Tap Changer Contacts

Figure 2c: Remaining Copper Sulfide that was Flaking off on Ring Around the Diverter Switch Compartment

FIGURE 2

In a few cases with ASTM D 1275B tests the deposits found on the test strips that were questionable if they were copper sulfide as they were a bit off color. A test for solubility in a 50% diluted concentrated hydrochloric acid revealed that the deposits were not copper sulfide indicating the importance of careful examination of the copper strips to avoid false positives. Hydrochloric acid will not dissolve copper sulfide but will dissolve organic compounds and sludge.

In 2004 ABB introduced the concept of the covered conductor deposition (CCD) test [6]. In this method a copper strip was covered with transformer paper and aged at an elevated temperature in a nitrogen-purged environment. The paper was then ranked by the amount of the copper sulfide deposit. The original tests was performed with nitrogen sparing to keep the oxygen content low, which seemed to promote more deposition on the paper and less on the copper. Further study reveled that the oxygen content was a factor in the deposition mechanism. Increasing the temperature causes the rate of oxygen consumption to increase and with a sealed system or restricted access to air the oxygen content is greatly reduced. Low oxygen combined with the high temperatures promotes more deposition on the copper and less on the paper insulation. These conditions can now be controlled to maximize the deposition process in the paper. Since these earlier studies, Doble and CIGRE Working Group A2-32 have developed quick CCD test methods. In our studies, we learned that less paper and a certain restricted flow of air resulted in the best performance. Different gauge needles were examined with a variety of oils, test times and temperatures before a standard set of conditions were decided on. For complete analysis in the Doble CCD test, two vials are used, one with a breathing tube and one sealed to make sure not to miss something under low oxygen conditions. In each tube is a small quantity of oil and a paper wrapped copper rod. This is shown in Figure 3.

Doble CCD Test
FIGURE 3

The tubes are aged for 4 days at 140°C and then the copper rods and paper are examined for evidence of corrosion. For the copper rods this means comparison to the ASTM D 130 standard, which is also used for comparison for the bare copper in ASTM D 1275 methods. Graying and blackening of the copper rod are the primary indications of corrosion. If either of the copper rods is deemed to characterize the oil as corrosive, then the oil is considered to have failed. In addition, the paper materials from both tubes are examined for deposits. There are many deposits that can form, but it is only those with a metallic film that are considered to be corrosive sulfur deposits and a failure of the oil in the test.

Many new and service-aged oils have since been tested using this Doble CCD method. With the breathing tubes there are many more deposits on the paper insulation than for the sealed ones, more than could be explained by corrosive sulfur. It became important to distinguish between deposits that were benign or have little effect on the paper electrical properties and those that were deleterious. To do this two methods were used, elemental analysis of the deposits for composition and electrical tests on the paper insulation.

To determine the elemental composition of the deposits further study was performed on paper samples using scanning electron microscopy (SEM) and energy dispersive x-ray analysis. The results were able to clearly show that the shiny films on the paper were copper sulfide deposits and that others deposits were comprised mostly of other aging byproducts. In cases where there were significant amounts of copper sulfide as seen by the metallic sheen and SEM/EDX tests, the dielectric breakdown voltage was often reduced below 50% of the control value. It is important to note that in some cases, even with the breathing tubes, the “fail” criterion is only exceeded on the copper rod. This is still considered to have failed, and is consistent with experience from the field.

Our experience has been that the breathing tube most often provides the best assessment of the oil, corresponding well with in-service experience and electrical tests on paper samples from laboratory-scale experiments. However, there is a high degree of overlap between the sealed and breathing tubes. The breathing tubes will more often have metallic deposits on the paper. Examples of metallic deposits from in-service apparatus and the Doble CCD test are given in Figure 4a-c.

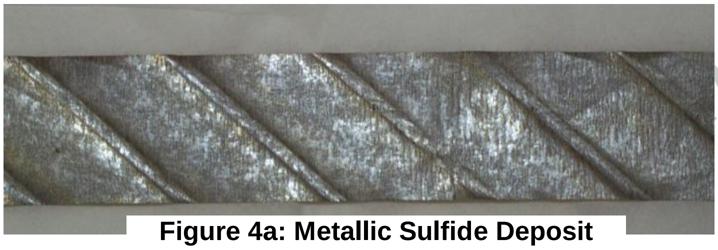


Figure 4a: Metallic Sulfide Deposit on Paper from Failed Winding

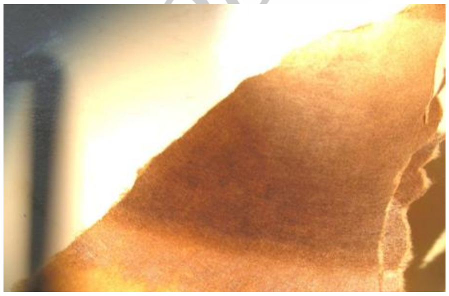


Figure 4b: Metallic Sulfide Deposit on Paper from Bushing

Figure 4c: Metallic Sulfide Deposite Paper from Doble CCD Test

FIGURE 4

In our view it is important to have tests that can provide a good evaluation of oils, relative to practical concerns about their long-term performance. Whenever there is accelerated aging, there is introduced some subjective evaluation concerning acceptable limits. This is particularly true with tests that have a visual observation component. However, there appears to be sufficient evidence that ASTM D 1275A is not adequate. A combination of ASTM D 1275B and the Doble CCD test are reasonable criteria to place on the manufacture of oils and provide improved corrosion resistance for their use in electric apparatus that should meet the present demand. If it is assumed that a 10°C temperature increase doubles the rate of reaction, then comparing temperatures and times the ASTM D 1275B is about five times more rigorous than ASTM D 1275A. The Doble CCD test is also about five times more rigorous than the ASTM D 1275A time, 19 hours versus 96 hours. This is even without including the effects of the copper being paper wrapped in the CCD test.

There have been a few cases where the ASTM D 1275B test and the Doble CCD test have shown that the oil was acceptable even though there was evidence of corrosion in the bushing or transformer. Although this seems counter intuitive, there is a reasonable explanation. Transformer oils have a limited amount of sulfur in them and an even more limited amount of corrosive sulfur. Once the corrosion process has gone on for some time, it is possible that for some oils most of the corrosive sulfur has reacted and formed deposits either on the conductor, in the paper or some combination of both. If the test on the oil is performed late in the process, there might not be enough corrosive sulfur left to fail the test. In the two cases we have seen that the oil passed the test even though there was clear evidence of corrosion, there was significant deposition on bare copper. In other cases the oil had failed the corrosive sulfur test even after failure of the equipment suggesting there was a larger reservoir or corrosive sulfur in these oils.

It is easy to make the case that new oils should meet the new corrosive sulfur requirements so as to not introduce the risk of excessive corrosion. It is desirable for new oils to meet the test requirements without the use of passivators that do not have a long-tem record of use in this application and which might become depleted with aging. Effective April 2, 2008 Doble changed its requirements for its Transformer Oil Purchase Specification (TOPS) to include the Doble CCD test. A copy of this is provided in the Appendix including the Doble CCD test method. We believe that use of these new methods going forward will prevent corrosive sulfur problems.

IN-SERVICE OILS

For in-service oils there is the need for risk assessment. It is easy if an in-service oil is tested and it passes both ASTM D 1275B and the Doble CCD test, as no action is required. This does not mean that there has not been any corrosion but rather that there will not be much corrosion going forward. However, if the oil fails the ASTM D 1275B or the Doble CCD test, what criteria should be used to assess the need for remedial action? Table 1 shows the criteria that can be used and what would be considered high/moderate/and low risk. As can be seen the risk is reduced if the oil passes the corrosive sulfur tests, the apparatus is operated at low temperatures with high oxygen contents in the oil and if a non-reactive metal or enameled-coated copper conductor is used. These criteria are not all sharply defined, as there is not enough experience with various oils to provide such guidelines. The bare copper test does not ranked as great of a concern as the CCD test as deposition in the paper is the most severe condition and only correctable by replacement of the windings. If the metal sulfides are deposited on bare metal surfaces in some cases it might not do any serious harm. If most of the copper sulfide is formed in this way, leaving in-sufficient amounts to form deposits in the paper, the unit could possibly have a long life.

TABLE 1
Risk Assessment for Corrosive Sulfur Failure Mechanism

Criteria	**Highest Risk**	**High Risk**	**Moderate Risk**	**Moderate Risk**	**Lower Risk**	**Lowest Risk**
Unit manufactured after 1998	X	X	X	X		X
Fail D1275B	X		X	X	X	
Fail Doble CCD test	X	X		X	X	
Operates at high temperatures over long times	X	X	X	X		X
Sealed oil expansion system or operates with low oxygen content	X	X	X	X		X
Bare copper conductors	X	X	X			X
Unit critical to system	X	X	X	X		X

Some of the oils that have been in transformers with corrosion problems have high amounts of dibenzyl disulfide (DBDS), in the low hundreds of parts per million (mg/kg). It has been established that the DBDS will breakdown at elevated operating temperatures and form mercaptan byproducts that are corrosive. In high oxygen environments the mercaptan can in part reform into DBDS. In lower oxygen environments the reactions favor corrosion reactions. This suggests that depletion of DBDS in transformers could be an indicator of corrosion, but there are other reactions that could also occur with the DBDS and aging byproducts so this requires further study. In testing of in-service equipment it appears that in some cases the DBDS concentration is quite steady while in other cases there has been a significant decline in the DBDS content. For those units where the DBDS is steadily declining consideration should be given to removal processes that strip out the DBDS, passivating or replacing the oil or both. Any corrosion that has taken place cannot be reversed if deposition has occurred in the insulating materials, but future reactions would be retarded.

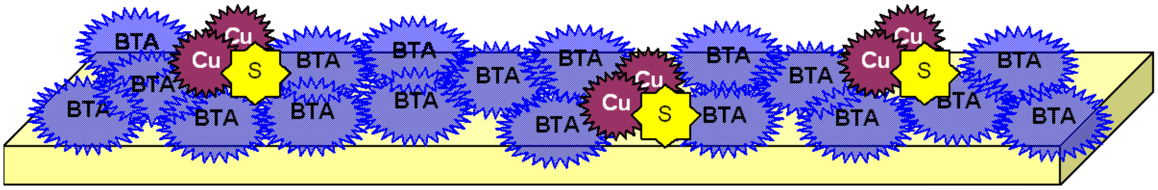
Laboratory tests were performed at 150°C under similar conditions as ASTM D 1275B with DBDS spiked into a “sulfur free” white oil. For tests performed with 50 – 250 ppm of DBDS the copper was corroded within 48 hours. With only 5 ppm of DBDS spiked in white oil corrosion occurred, but it took over 100 hours before the copper strip was considered a “fail”. It is of interest that oils with similar amounts of DBDS can behave differently in corrosive sulfur tests suggesting there are other molecules that influence the corrosion process.

It should be noted that there have been corrosive sulfur problems with oils that did not contain detectable amount of DBDS and that other sulfur compounds are of concern.

REMEDIAL ACTIONS

It has been observed in some of our studies that addition of traditional antioxidant and depletion of polar compounds can improve corrosion resistance. In some cases, the introduction of 2,6-ditertiary butyl paracresol (DBPC) has been the difference between oils passing and failing corrosion tests. In many cases, clay treatment to remove acids and some other polar compounds will not improve an oil’s corrosive sulfur test performance. In some cases though, probably where the oil has a more limited amount of corrosive sulfur compounds, the clay treatment can be beneficial. Both the influence of antioxidant and clay treatment suggest that corrosion and deposition processes have some intermediate steps involving copper surface chemistry and transport that are influenced by a more complex chemistry than just that driven by the concentration of corrosive sulfur compounds.

The most widely used remedial action for the corrosive sulfur problem has been to use a passivator. The two most widely used for this application to date have been benzotriazole (BTA) mostly used as an anti-static agent and to retard oxidation and Irgamet® 39 a derivative of benzotriazole used to improve resistance to oxidation and prevent corrosion. These passivators react with the metal surface and metal ions to form stable films on the surface or stable compounds that retards the attack by corrosive sulfur compounds as shown in Figure 5.

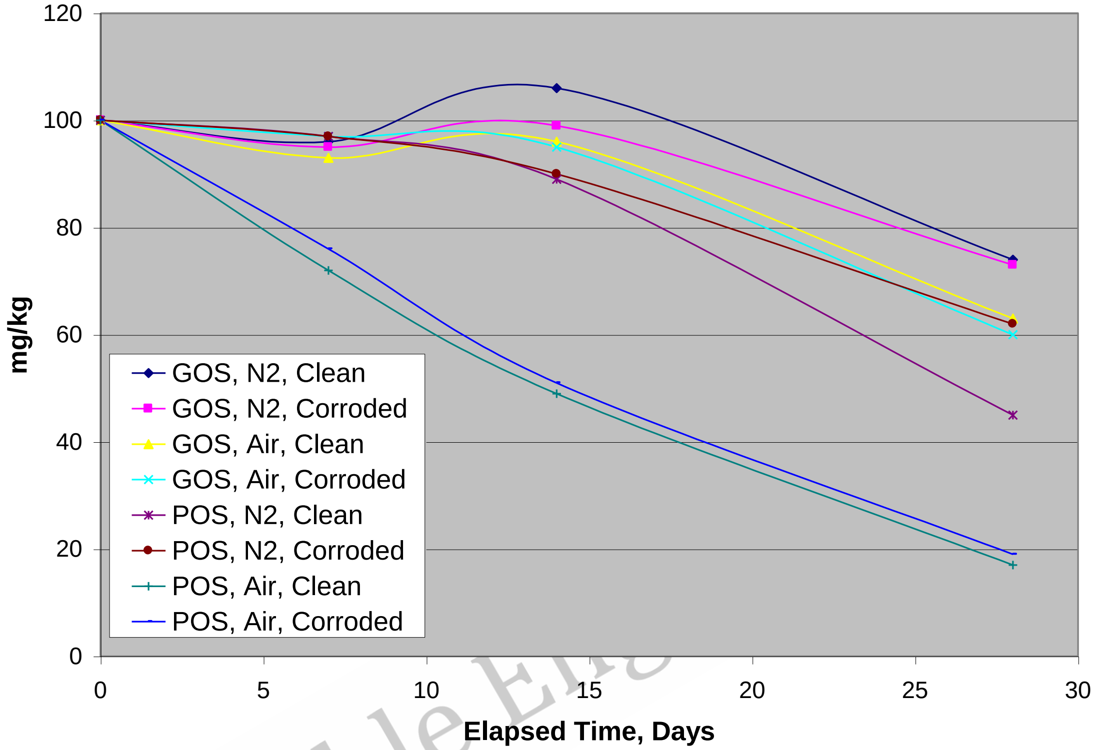


Passivation of Copper Surface
FIGURE 5

These two passivators have been subject to considerable study for use in transformers. In these studies two minor issues have been found. One is that with some base oils there can be some stray gassing with the addition of the passivator. The stray gassing behavior primarily consists of the generation of hydrogen and carbon dioxide for some limited time. In laboratory scale experiments the hydrogen increase can be quite high in a short period of time, from 100's to over 1000 ppm of hydrogen in some cases. However, in service stray gassing has been indicated as a possible source of hydrogen generation only in a few cases, and seems to increase to about 100 ppm or a little above this and then stops. This gassing behavior, the generation of hydrogen could be indicative of partial discharge behavior and should therefore be monitored in gassing transformers to verify the nature of the problem. A continuing or extensive gassing problem is likely to be more serious than stray gassing.

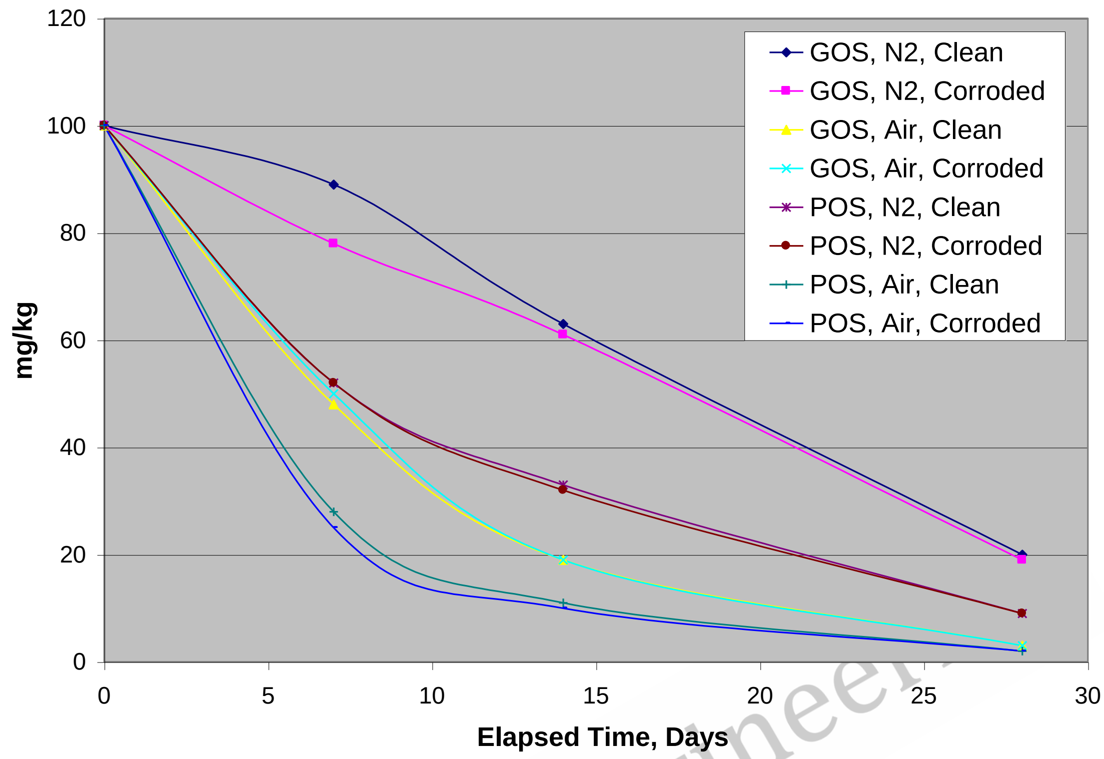
There is no question that passivators retard the corrosion reactions between sulfur compounds and reactive metal components. It would appear that the passivator also retards formation of deposits of metal sulfides in the paper insulation. The question becomes, how effective is the passivator over the life of transformers that can operate for many decades? Transformer failures from corrosive sulfur have occurred after less than one year in service, but mostly after several years. To be considered corrective for a lifetime, passivator should show at least an order of magnitude improvement in its time-temperature characteristics for excessive corrosion to occur.

Figure 6 shows passivator depletion on two oils studied under laboratory conditions. The oils were from units that failed from corrosive sulfur, forming copper sulfide deposits in the paper insulation. One oil had somewhat better oxidation stability results based on traditional tests. The better oxidation stability oil was labeled as Good Oxidation Stability" (GOS) and the other as "Poor Oxidation Stability" (POS). Both oils we passivated with Ciba Irgamet 39 at a concentration of 100 ppm. Some tubes had the oil purged with nitrogen, which reduces the oxygen content to a low concentration. In other tubes the oil was purged with air to start. A bare copper strip was aged in the oil in all tubes that were sealed. The copper was from a failed transformer that was in the later stages of corrosion based on the discoloration, 3a by ASTM D 130. In some tubes the copper surface was cleaned to remove any corrosion or oxides or aging byproducts. Other tubes contained copper cleaned only to remove the oil. The aging was performed at 80°C, which is typical of normal operating temperatures for some transformers. The results show that the passivator is depleted in all cases but that with the oil with the poorer oxidation stability the passivator is depleted more quickly suggesting that there might be additional reactions than passivation of the copper surface. Some oils showed a small amount of depletion that could be associated with passivation reactions with the copper. None of the cooper strips were deemed corroded.



Passivator in Oil Depletion with Aging at 80°C
FIGURE 6

Other similar tests were performed at higher temperatures, 110 and 150°C. The temperature of 110°C was chosen in part because it represents the expected hottest-spot temperature for a transformer with thermally upgraded insulation, loaded and operating at full rated conditions. At 110°C some clear patterns developed, as seen in Figure 7. The oils that were purged with nitrogen, regardless of the copper material or oil oxidation stability, had a slower depletion rate of the passivator. Even though the passivator was greatly reduced in these nitrogen purged vessels, the copper strip still “passed” after more than 185 days of aging. The oils that were started aging after being saturated with air did not perform nearly as well. The passivator depletion from the oil was quicker and by 30 days it appears it would have been mostly or all gone from the oil. Here the largest factor was the oxygen content at the start of the test. It appears the initial high oxygen content has a significant effect on both the depletion of the passivator and the corrosion process. The corrosion appeared to start soon after the passivator was close to being depleted from the oil.



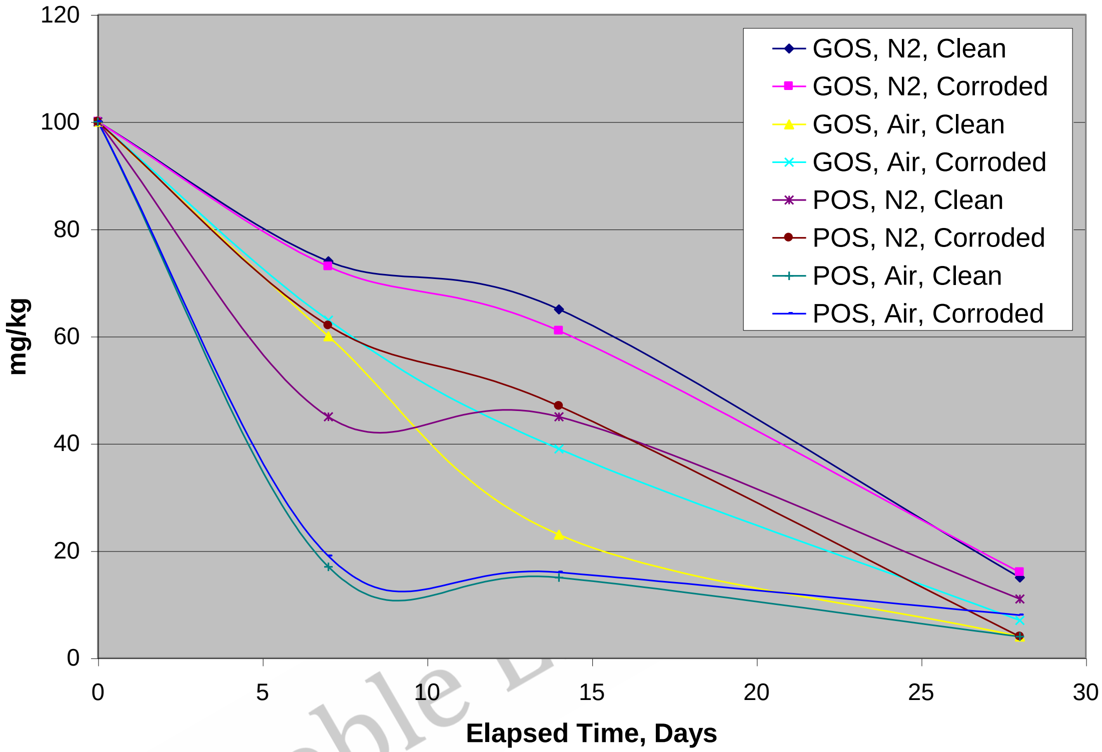
Passivator in Oil Depletion with Aging at 110°C
FIGURE 7

Table 2 shows the time to heavy corrosion or a "fail" would occur. It is evident that for the oils that were initially high in oxygen content that corrosion started close to the time the oil was depleted of passivator. For the copper that was pre-corroded the time to heavy corrosion was within a few days of the passivator being mostly depleted, while the clean copper seemed to take a few weeks to reach the same condition. This suggests that the passivator in the oil is important to continually provide molecules to hinder the reaction of corrosive sulfur with metal surfaces. When passivators are used the content in the oil should be monitored and before being depleted, replenished. In addition, if the passivator is added after the corrosion process is advanced, the margin of safety can be small.

TABLE 2
Corrosion with Passivated Oil

Copper Type	Starting Atmosphere	Oil Type	Time to Heavy Corrosion, Days
Clean	Nitrogen	GOS	>185
Corroded	Nitrogen	GOS	>185
Clean	Air	GOS	45
Corroded	Air	GOS	32
Clean	Nitrogen	POS	>185
Corroded	Nitrogen	POS	>185
Clean	Air	POS	43
Corroded	Air	POS	30

At 150°C a somewhat different story emerged. The non-passivated oil used for this study failed the ASTM D 1275B corrosive sulfur test, which is for 2 days at 150°C so the passivator certainly improved the performance over the base oil characteristics. Even though the passivator was still present after 5-7 days of aging there was significant copper sulfide on all strips. The depletion of the passivator at 150°C seemed to be similar to the rate at 110°C but the effectiveness was not as good at the higher temperature (Figure 8).



Passivator in Oil Depletion with Aging at 150°C
FIGURE 8

It is concluded that the use of passivators is helpful in retarding reactions involving corrosive sulfur and reactive metals in transformers. They should be used to reduce risk as applicable with in-service oils. However, the oil should be monitored to maintain active protection. More research is needed to provide more evidence of the long-term effectiveness of passivation. In addition, it is important to verify that the passivator is effective for each oil. In a recent test of in-service oils that had been passivated, one with a concentration of Irgamet 39 of over 100 ppm, failed the ASTM D 1275B and Doble CCD test. On the CCD test there was a metallic film formed on the paper in the breathing tube and in the sealed tube the copper rod had a black deposit. In this case the passivator would not appear to be adequately protective at this concentration.

If the passivator content cannot be tested, such as for bushing applications they should not be used.

Other methods of remedial action such as removal of some of the corrosive sulfur compounds [18, 19] and oil replacement [7] are under study.

CONCLUSIONS

For new transformers oils two tests for corrosive sulfur are recommended and these are included in the April 2, 2008 edition of the Doble Transformer Oil Purchase Specification. The test methods are ASTM D 1275B and the Doble CCD test. These two tests have similarities with bare copper and copper sulfide deposits in paper failure modes respectively. These tests can be applied with in-service oils and some guidelines for determining units at risk have been provided. Passivators in oil can be used to reduce risk but there remains some evidence that the long-term effectiveness requires further study.

REFERENCES

[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 Conference of Doble Clients*, Boston, MA, Insulating Materials Session, 2005.

[3]. Claiborne, C., Dahlund, M., Gustafsson, K, Hajek, J., and Hjortsberg, A., "Specification 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.

[5]. Troisi, J., "Failure of a 450-MVA Autotransformer with Load Tap Changer in the Main Tank, Proceedings of the 2001 International Conference of Doble Clients", Sec 8-14, 2001.

[6]. Hajek, J., Dahlund, M., and Pettersson, L., "Quality of Oil Makes the Difference, ABB Discovers the Solution to Transformer Breakdowns", ABB Review, Nr.3-2004, pp. 61-63, ABB ltd., Zurich, Switzerland, 2004.

[7]. Griffin, P. J., and Lewand, L. R., "Understanding Corrosive Sulfur Problems in Electric Apparatus', *Proceedings of the Seventy-forth Annual Conference of Doble Clients*, Boston, MA, Insulating Materials Session 1, 2007.

[8]. Oommen, T. V., Corrosive and Non-corrosive Sulfur in Transformer Oils", Electrical/Electronics Insulation Conference, Chicago, October 4-7, 1993

[9]. Rocha, A. H., " Faults in 500-kV Shunt Reactors Caused by Corrosive Sulfur in the Insulating Oil", *Proceedings of the Sixty-eighth Annual Conference of Doble Clients*, Boston, MA, Section 5-4, 2001.

[10]. Scatiggio, F., Marchiori, C. and Botelho, P., Understanding and Management of Sulfur Corrosion from Insulating Oil", *Proceedings of the Seventy-forth Annual Conference of Doble Clients*, Boston, MA, Insulating Materials Session 2, 2007.

[11]. Pankratz, C., "Utilities Perspective on Testing for and Management of Corrosive Sulfur in Transformer Fleets, Part A", *Proceedings of the Seventy-forth Annual Conference of Doble Clients*, Boston, MA, Insulating Materials Session 3A, 2007.

[12]. McCulla, G., “Utilities Perspective on Testing for and Management of Corrosive Sulfur in Transformer Fleets, Part B”, *Proceedings of the Seventy-forth Annual Conference of Doble Clients*, Boston, MA, Insulating Materials Session 3B, 2007.

[13]. Asano, R., Miethke, B. R. W., and McIver, J., “Siemens Experience on Passivated Oils”, *Proceedings of the Seventy-forth Annual Conference of Doble Clients*, Boston, MA, Insulating Materials Session 4, 2007.

[14]. Claiborne, C., Frimpong, G., Ball, W., and Hjortsberg, A., “Transformer Oils, Corrosive Sulfur and Effects on Transformers”, *Proceedings of the Seventy-forth Annual Conference of Doble Clients*, Boston, MA, Insulating Materials Session 5, 2007.

[15]. Pahlavanpour, B., Odelius, H., and Sundkvist, K., “Corrosive Sulfur Issues and Remedial Actions”, *Proceedings of the Seventy-forth Annual Conference of Doble Clients*, Boston, MA, Insulating Materials Session 6, 2007.

[16]. Null, V., “Evaluation of Potentially Corrosive Sulphur in Electrical Oils”, *Proceedings of the Seventy-forth Annual Conference of Doble Clients*, Boston, MA, Insulating Materials Session 7, 2007.

[17]. Rasco, J., “Petroleum Refining Production of Naphthenic Transformer Oil Control of Corrosive Sulfur”, *Proceedings of the Seventy-forth Annual Conference of Doble Clients*, Boston, MA, Insulating Materials Session 8, 2007.

[18]. Dominelli, N., Kovacevic, S., Hall, E. and Lau, M., “Corrosive Sulfur in Transformers – Its Presence, Fate, and Removal”, *Proceedings of the Seventy-forth Annual Conference of Doble Clients*, Boston, MA, Insulating Materials Session 9, 2007.

[19]. Lewand, L. R., and Reed, S. “Destruction of Dibenzyl Disulfide in Transformer Oil” *Proceedings of the Seventy-fifth Annual Conference of Doble Clients*, Boston, MA, Insulating Materials Session, 2008.

AUTHOR BIOGRAPHIES

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.

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 and member of the US National Committee for IEC TC10.

APPENDIX: DOBLE TRANSFORMER OIL PURCHASE SPECIFICATION

(Developed Under the Auspices of the Doble Oil Committee)

Revised April 2, 2008

COMPOSITION

Insulating oils for general applications, which are covered by this specification, are manufactured from predominantly naphthenic base crudes. Distillates from these crudes may be acid refined, hydrogen treated, solvent extracted, or processed by other suitable refining methods to yield acceptable mineral insulating oils which meet the test requirement at the point of delivery.

Oils from paraffinic crudes may also be covered by this specification with the exception of performance at low temperatures. Other requirements may be needed for these products to ensure proper function at low temperatures.

ADDITIVES

The use of all additives must be identified. An additive is a suitable chemical substance, which is deliberately added to a mineral insulating oil to improve certain characteristics.

Oxidation stability

Uninhibited oils must be free of additives, either natural or synthetic that are used to improve oxidation stability. This includes but is not limited to 2,6 ditetiary-butyl phenol, 2,6 dietertiary-butyl cresol, or metal deactivators such as benzotriazole and its derivatives.

Inhibited oils are insulating oils, which have been supplemented with either 2,6 ditetiary-butyl phenol or 2,6 dietertiary-butyl cresol or any other specified and acceptable oxidation inhibitor. If an additive other than 2,6 ditetiary-butyl phenol or 2,6 dietertiary-butyl cresol is used, appropriate limit values for oxidation stability tests (those for Type I or Type II oils) should be agreed to by the purchaser and seller. If more than one additive is used, the more stringent limits for oxidation stability, those for the Type II oils would apply.

Pour point depressants, gassing tendency improvers, additives for corrosive sulfur and static electrification (metal passivators), antifoaming agents and other additives

All additives should be specifically identified or at a minimum identified by class of compounds such as metal passivator if the specific information is proprietary.

PRODUCTION AND SHIPPING

Insulating oils covered by this specification shall be produced from proven crudes by suitable refining techniques, both of which shall have been approved by the purchaser. After such approval, no change in crude source, processing, or refining methods shall be made that results in a substantial change in the product characteristics without the prior approval of the purchaser.

Shipping containers should be dedicated to new transformer oils. The shipping method and containers shall be agreed upon by purchaser and seller and shall not be changed without prior approval of the purchaser.

TRANSFORMER OIL PURCHASE SPECIFICATION - TEST LIMITS

TYPE OF TEST	ASTM METHOD	UNINHIBITED	INHIBITED	
			TYPE I	TYPE II
Aniline Point, °C	D 611	63 min	63 min	63 min
Carbon Type Composition % Aromatics, % Naphthenics, % Paraffinics	D 2140	No limits	No limits	No limits
Color (a)	D 1500	0.5 max	0.5 max	0.5 max
Corrosive Sulfur	D 1275B Doble CCD (b)	Non-corrosive	Non-corrosive	Non-corrosive
Dielectric Breakdown, kV	D 877	30 min	30 min	30 min
Dielectric Breakdown, kV	D 1816 (0.04" gap)	20 min	20 min	20 min
Water Content, ppm (as received)	D 1533	30 max	30 max	30 max
Flash Point, °C	D 92	145 min	145 min	145 min
Furanic Compounds(c) (optional test)	D 5837	25 µg/L max	25 µg/L max	25 µg/L max
Impulse Breakdown Voltage, kV @ 25°C (d)	D 3300	145 min	145 min	145 min
Interfacial Tension, dynes/cm, 25°C	D 971 (unfiltered)	40 min	40 min	40 min
Neutralization Number, mg KOH/g	D 974 (modified) (e)	0.015 max	0.015 max	0.015 max
Pour Point, °C	D 97	-40 max	-40 max	-40 max
Power Factor, 100°C, %	D 924	0.30 max	0.30 max	0.30 max
Power Factor, 25°C, %	D 924	0.05 max	0.05 max	0.05 max
Specific Gravity, 60/60	D 1298	0.910 max	0.910 max	0.910 max
Viscosity: Kinematic cSt, 100°C 40°C 0°C	D 445	max. 3.0 11.0 76.0	max. 3.0 11.0 76.0	max. 3.0 11.0 76.0
Oxidation Inhibitor Content, % by wt.	D 2668 or D 4768 (f)	0.00 max	0.08 max	0.3 max
Sludge-Free Life (SFL) measured at 8-hr periods, hrs, ±8 hrs.	(Doble Procedure) (g)	40 min	64 min	80 min
Power-Factor Valued Oxidation (PFVO) (optional test)	(Doble Procedure) (g)	See graph for limit curve.	See graph for limit curve.	See graph for limit curve.
Oxidation Stability (acid sludge) 72 hours: % sludge by wt. Total acid no., mg KOH/g	D 2440	 0.15 max 0.5 max	 0.15 max 0.5 max	 0.1 max 0.3 max
164 hours: % sludge by wt. Total acid no., mg KOH/g		0.3 max 0.6 max	0.3 max 0.6 max	0.2 max 0.4 max
Oxidation Stability (Rotating Bomb), minutes	D 2112	Not Applicable	195 min	220 min
Polychlorinated Biphenyls	D 4059	ND (h)	ND (h)	ND (h)
OPTIONAL TEST Gassing Tendency Under Electrical Stress, micro L/min @ 80°C, hydrogen	D 2300	negative (i)	negative (i)	negative (i)

NOTES

(a) Oil must be clear and bright.

(b) Doble has developed a covered conductor deposition test (CCD) to detect excessive amounts of corrosive sulfur that could deposit in the paper insulation. A copy of the method is provided with this specification. When metal passivators are used, it is strongly recommend that the base oil meet the modified corrosive sulfur test before passivation.

(c) The test is for five furanic compounds, 5-hydroxymethyl-2-furfural, furfuryl alcohol, 2-furfural, acetyl furan, 5-methyl-2-furfural. The limit of 25 µg/L maximum applies to each compound.

(d) Needle negative to sphere grounded, 1-in (25.4-mm) gap.

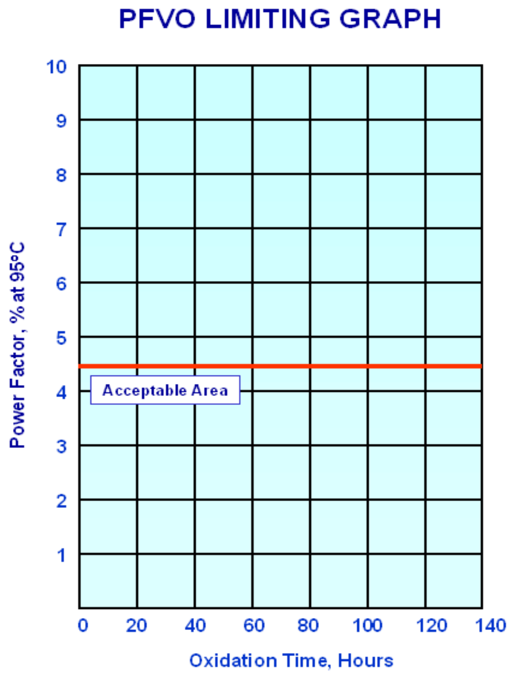
(e) Neutralization number is measured by using 1/100 normal potassium hydroxide standard alcoholic solution.

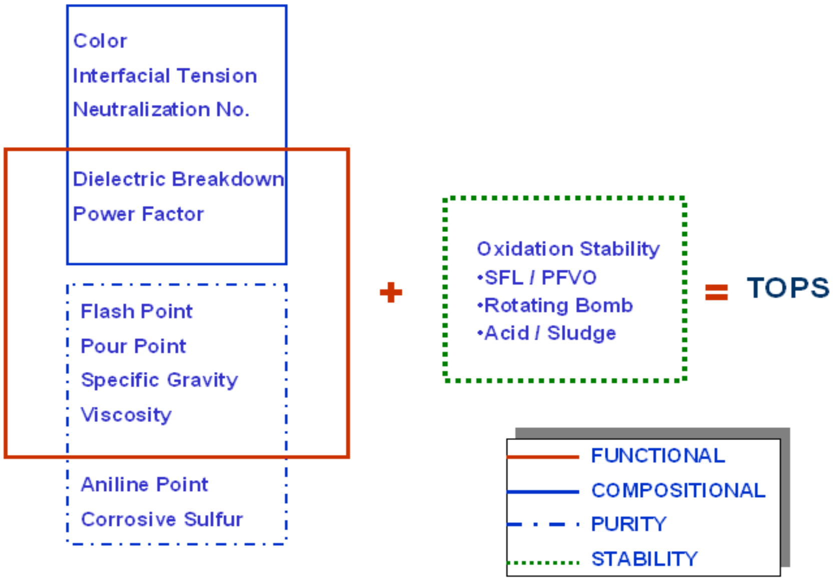
(f) Both 2,6-ditertiary butyl-paracresol and 2,6-ditertiary butyl-phenol have been found to be suitable oxidation inhibitors for use in oils meeting this specification.

(g) Sludge-Free Life and Power Factor Valued Oxidation (PFVO) tests are performed utilizing Doble Methods. The Sludge-Free Life of an oil, sampled at 8-hour intervals, is the number of hours which have elapsed between the start of the test and the time of taking the last sample which showed a sludge-free precipitation test.

(h) ND = none detected.

(i) The characteristic is positive if gas is evolved under the conditions of the test, and negative if gas is absorbed.





DOBLE TRANSFORMER OIL PURCHASE SPECIFICATION CHART

SIGNIFICANCE OF TESTS

The following comments and interpretations, based on both technical understanding as well as empirical knowledge, emphasize those properties which are functionally important to transformer oils:

Aniline Point (D 611) The aniline point is the temperature at which a mixture of aniline and oil separates. It provides a rough indication of the total aromatic content, and relates to the solvency of the oil for materials that are in contact with the oil. The lower the aniline point, the greater the solvency effect.

Carbon Type Composition (D 2140) The carbon type composition characterizes an insulating oil in terms of the percentage of aromatic, naphthenic, and paraffinic carbons. It can be used to detect changes in oil composition and to relate certain phenomena that have been demonstrated to be related to oil composition.

Color (D 1500) The color of a new oil is generally accepted as an index of the degree of refinement. For oils in service, an increasing or high color number is an indication of contamination, deterioration, or both.

Corrosive Sulfur (D 1275) This test detects the presence of objectionable quantities of elemental and thermally unstable sulfur-bearing compounds in an oil. When present, these compounds can cause corrosion of certain transformer metals such as copper and silver.

Dielectric Breakdown (D 877, D 1816) The dielectric breakdown is the minimum voltage at which electrical flashover occurs in an oil. It is a measure of the ability of an oil to withstand electrical stress at power frequencies without failure. A low value for the dielectric-breakdown voltage generally serves to indicate the presence of contaminants such as water, dirt, or other conducting particles in the oil.

Method D 1816 is more sensitive than Method D 877 to contaminants that lower the dielectric-breakdown voltage and is the preferred method for assessing the intrinsic breakdown strength of an oil.

Water Content (D 1533) A low water content is necessary to obtain and maintain acceptable electrical strength and low dielectric losses in insulation systems.

Flash Point (D 92) The flash point is the minimum temperature at which heated oil gives off sufficient vapor to form a flammable mixture with air. It is an indicator of the volatility of the oil.

Furanic Compounds (D 5837) Furanic compounds are generated as byproducts of the degradation of cellulosic materials such as insulating paper, pressboard, and wood. These compounds serve as indicators of insulation degradations. Because they are dissolved in the oil, furanic compounds can readily be sampled and tested by high performance liquid chromatography (HPLC). No significant quantity should be detected in new oils.

Impulse Breakdown Voltage (D 3300) The impulse breakdown voltage is the voltage at which electrical flashover occurs in an oil under impulse conditions. It indicates the ability of an oil to resist transient voltage stresses such as those caused by nearby lightning strokes and high-voltage switching surges. The results are dependent on electrode geometry, spacing, and polarity.

Interfacial Tension (D 971) The interfacial tension of an oil is the force in dynes per centimeter required to rupture the oil film existing at an oil-water interface. When certain contaminants such as soaps, paints, varnishes, and oxidation products are present in the oil, the film strength of the oil is weakened, thus requiring less force to rupture. For oils in service, a decreasing value indicates the accumulation of contaminants, oxidation products, or both. It is a precursor of objectionable oxidation products that may attack the insulation and interfere with the cooling of transformer windings.

Neutralization Number (D 974) The neutralization number of an oil is a measure of the amount of acidic or alkaline materials present. As oils age in service, the acidity and therefore the neutralization number increases. A used oil having a high neutralization number indicates that the oil is either oxidized or contaminated with materials such as varnish, paint, or other foreign matter. (A basic neutralization number results from an alkaline contaminant in the oil.)

Pour Point (D 97) The pour point is the lowest temperature at which oil will just flow. A low pour point is important, particularly in cold climates, to ensure that the oil will circulate and serve its purpose as an insulating and cooling medium. It may be useful for identifying the type (naphthenic, paraffinic) of oils.

Power Factor (D 924) The power factor of an insulating oil is the cosine of the phase angle between a sinusoidal potential applied to the oil and the resulting current. Power factor indicates the dielectric loss of an oil; thus the dielectric heating. A high power factor is an indication of the presence of contamination or deterioration products such as moisture, carbon or other conducting matter, metal soaps and products of oxidation.

Specific Gravity (D 1298) The specific gravity of an oil is the ratio of the weights of equal volumes of oil and water determined under specified conditions. In extremely cold climates, specific gravity has been used to determine whether ice, resulting from the freezing of water in oil-filled apparatus, will float on the oil and possibly result in flashover of conductors extending above the oil level. The specific gravity of mineral oil influences the heat transfer rates. Oils of different specific gravity may not readily mix when added to each other and precautions should be taken to ensure mixing.

Oxidation Inhibitor Content (D 2668, D 4760) These tests provide a method for the quantitative determination of the amount of oxidation inhibitor (2,6-ditertiary butyl-paracresol or 2,6 ditertiary phenol) present in an inhibited oil. Control of the inhibitor content is an important factor in maintaining long service life of inhibited insulating oils.

Power Factor Valued Oxidation (PFVO) This test, developed by the Doble Engineering Company, periodically measures the power factor of an oil while it is being aged at 95°C in the presence of copper and air. Consequently, it indicates the dielectric-loss characteristics of insulating oil as a function of accelerated aging conditions. The resulting graph of power factor versus time characterizes a given oil. It is applicable as a continuity test, as well as a measure of oil quality. The test is run concurrently with the Doble Sludge-Free Life test that measures the time until the oil forms sludge.

Oxidation Stability (acid/sludge) (D 2440) The acid/sludge test is a method of assessing the oxidation resistance of an oil by determining the amount of acid/sludge products formed when tested under certain prescribed conditions. Oils which meet or exceed the requirements tend to preserve insulation system life and ensure acceptable heat transfer. The test may also be used to check the performance consistency of this characteristic of production oils.

Oxidation Stability (D 2112) This test is a rapid method for the evaluation of the oxidation stability of new insulating oils containing an oxidation inhibitor. It is used as a control test for evaluating the response characteristics of new oils to oxidation inhibitors. It may also be used to check the performance consistency of production oils. Good oxidation stability is a principal requirement for long service life of transformer oils.

Gassing Under Electrical Stress (D 2300) The gassing tendency is defined as the rate of gas evolved or absorbed by an insulating oil when subjected to electrical stress of sufficient intensity to cause ionization. The characteristic is positive if gas is evolved and negative if gas is absorbed. Correlation of results with equipment performance is limited at present.

Polychlorinated Biphenyls (D 4059) Regulations prohibiting the commercial distribution of polychlorinated biphenyls (PCBs) mandate that insulating oils be examined for PCB contamination levels to assure that new products do not contain detectable amounts.

Viscosity (D 445) Viscosity is the resistance of oil to flow under specified conditions. The viscosity of oil used as a coolant influences heat transfer rates and consequently the temperature rise of an apparatus. The viscosity of an oil also influences the speed of moving parts in tap changers and circuit breakers. High viscosity oils are less desirable, especially in cold climates. Standard viscosity curves can be generated using Method D 341 by measuring two or three data points and plotting the data on special chart paper. The resulting curve can be used to interpolate or extrapolate values at temperatures where the viscosity is not measured directly.

Doble Method for the Determination of Copper and Copper Sulfide Deposition Using the Covered Conductor Deposition (CCD) Test

Note: Parts of the ABB and Siemens CCD testing protocols described in CIGRE WG A2-32 April 2006 round robin test protocol were used for this test method.

1. Scope

1.1 This test method describes the detection of corrosive sulfur compounds (both inorganic and organic) in electrical insulating oils and the propensity of such oils to form deposits either on copper or in Kraft paper insulation (non-thermally upgraded cellulose).

1.2 Mineral insulating oils may contain substances that cause corrosion under certain conditions of use. This test method is designed to detect the presence of free sulfur and corrosive sulfur compounds by subjecting copper and Kraft paper insulation to contact with oil under prescribed conditions.

1.3 Although designed for mineral oil of petroleum origin and Kraft paper insulation, different insulating oils and other types of insulation can be used.

2. Apparatus

2.1 Oven—A hot-air oven provided with suitable means of heating to, and controlling at, 140 ± 2°C. A circulating hot-air oven is preferred.

2.2 Containers—Glass headspace vials with bevel, 20 mL, 23mm diameter x 75mm height. Slight variations in volumes and sizes are allowed as these will vary depending on the manufacturer.

2.3 Vial Caps – Aluminum seal with TFE liner/butyl rubber septa, 20mm diameter

2.4 Aluminum-Heating Block – constructed of solid aluminum to hold vials at constant temperature while in oven (see Appendix X1 for details)

2.5 Needles, 18-gauge – made of stainless steel with deflected point, ≈ 3.8cm long (1.5 inches)

3. Materials

3.1 Copper Rod, 99.99+% pure – Alloy 101, ≈ 3.9878 mm (0.1570 inch (5/32)) diameter, of sufficient length to cut into 5cm lengths.

3.2 Kraft paper – with the following characteristics:

Thickness	≈ 0.0762mm (0.0711-0.0813), 3 mil (0.003 inches), 2.8-3.2 mil
Density	0.70 – 0.85 g/cm3
Width	≈ 1.25cm (0.5 inches)
Air Permeability	0.5 – 1 um/Pa*s (H)
Conductivity	< 4 mS/m
Nitrogen Content	< 50 mg/kg
Copper Content	< 50 mg/kg

3.3 Aluminum Wire, 20AWG, alloy 1100

3.4 Abrading Material, consisting of 240-grit silicon carbide paper or cloth

3.4 Polishing Material, consisting of 400-grit silicon carbide paper or cloth

3.5 Laboratory Tissue

4. Reagents

4.1 *Acetone*, cp.

4.2 *Pentane*, cp.

4.3 *White Oil*-mineral oil refined in such a manner as to have an extremely low total sulfur content (less than 5 mg/kg per ASTM Method D 4294). Test oil that is going to used per ASTM D 1275B to make sure it is non-corrosive.

5. Summary of Test Method

5.1 An abraded and polished copper rod is wrapped with a single layer of Kraft paper in a diagonal fashion. The copper rod is cut at 5cm lengths. Two copper rods are required for each test and one rod is placed in each vial. In one vial, 16 mL of oil is added, the vial is capped and crimped and an 18-gauge needle is inserted through the septum to about 1cm below the septum surface.

5.2 In the second vial to which the paper-wrapped copper rod has already been added, 16mL of oil is added. The vial is then capped and crimped.

5.3 Both vials are placed in the aluminum heating block and placed in an oven controlled to 140 ± 2°C for 4 days (96 h).

5.4 After 4 days the vials are removed, allowed to cool and the test specimen vials decrimped.

5.5 The paper wrapped copper rods are then removed from the oil, unwrapped from the copper and both the copper and paper are washed with an hydrocarbon solvent until all the oil is removed. The paper and the copper rod from both vials are inspected for deposits and the results reported.

6. Preparation of Apparatus

6.1 Use headspace vials directly from the manufacturer. Do not reuse vials and do not store them in areas where possible contamination can occur. Two vials are required for each test.

6.2 To one vial, add a 5cm long Kraft paper covered copper rod that has been prepared in the following manner:

6.2.1 Secure the copper rod in a vise or similar apparatus.

6.2.2 Abrade the copper rod with 240-grit paper or cloth until the copper is bright and shiny.

6.2.3 Polish the copper rod with 400-grit paper or cloth until the copper surface is relatively smooth.

6.2.4 Clean the copper rod with laboratory tissue slightly wetted in acetone by wiping the area abraded and polished in a length-wise fashion making sure the entire diameter of the rod is clean.

6.2.5 Allow the copper rod to air dry before wrapping it with Kraft paper insulation.

6.2.6 Using the 0.5 inch wide Kraft paper specified in Section 3.2, wrap it onto the copper rod at about a 30° angle from horizontal starting at one end of the copper rod. After a few wraps, secure one end of the paper to the copper rod with 20 AWG aluminum wire. Continue to wrap the paper around the copper rod. A slight overlap is acceptable. Once the strip of paper is used up or the overlap is greater than 3mm, discontinue the wrapping and secure the other end with aluminum wire.

6.2.7 Lightly mark paper wrapped copper rod at 5cm lengths with a graphite pencil.

6.2.8 On either side of the mark, secure the paper to the copper rod using the aluminum wire.

6.2.9 Once the paper is secured, cut the rod at the pencil marks. Additional paper wrapped cut rods can be stored for future use in an air-tight container with the rods stored under nitrogen.

6.3 After the rod has been added to the headspace vial, add 16mL of oil from the sample. Do not process the oil in any manner. Using an appropriate tool, seal the 20-mL vial using the aluminum caps fitted with a TFE-fluorocarbon-faced butyl septum. Ensure that the lined side is turned towards the inside of the vial and check that the vial is properly sealed by trying to turn the cap. If the cap is not tightly fixed, repeat the process.

6.4 Insert the 18-gauge needle into the middle of the septum and through it to a depth of about 1cm below the septum. Place the prepared vial into the aluminum heating block. This is the air ingress vial.

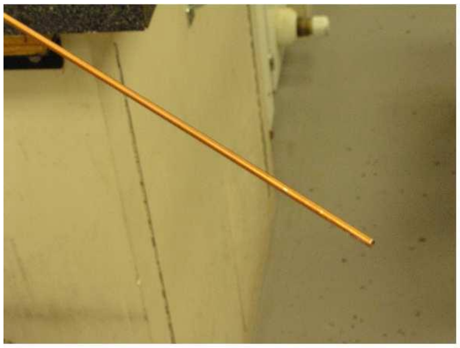
6.5 To a second vial, add another paper wrapped copper rod. Add 16mL of air saturated oil to the vial. If unknown if the oil is air saturated, place 25mL of oil in a 50mL beaker and let stand for 30 minutes before adding the correct volume to vial. Once the oil is added, secure the vial cap as described in Section 6.3. Place the prepared vial into the aluminum-heating block. This is the sealed vial.

6.6 Reference test specimens consisting of 16mL of white oil and paper wrapped copper rod, as described in this Section, are to be prepared in both "air ingress" and "sealed" vials. They are to be used in the following circumstances:

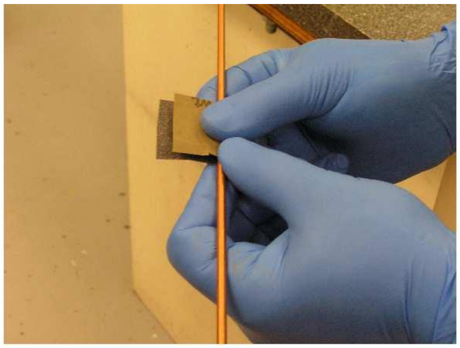
6.6.1 Method Validation – when initially setting up this method it is important to make sure that no false positives are obtained. Results of the testing are to indicate that the copper is "non-corrosive" as defined in Section 8.1 and the paper has "no deposits" as defined in Section 8.2.

6.6.2 Compatibility of Materials – During the course of performing this method, there may be changes in origins of the copper, vials, paper and caps. In all cases, these materials should be tested using reference test specimens to ensure that none of them contain materials and compounds that may affect the test.

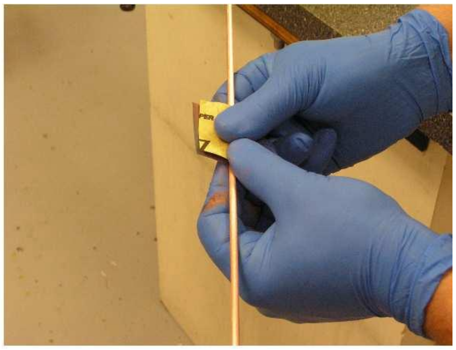
6.6.3 Referee Samples-To be tested and analyzed along with the regular test specimens as a condition of the test when requested.



Section 6.2.1



Section 6.2.2

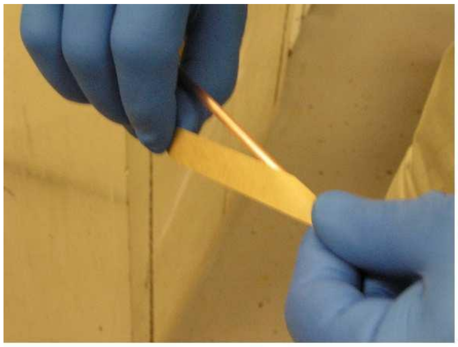


Section 6.2.3

Section 6.2.4, Part 1

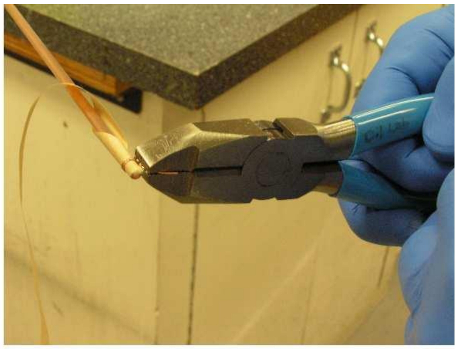
Section 6.2.4, Part 2

Section 6.2.4, Part 3

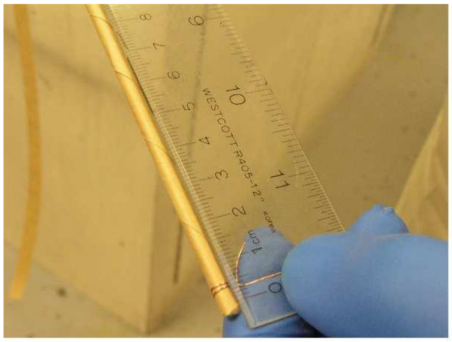


Section 6.2.6, Part 1

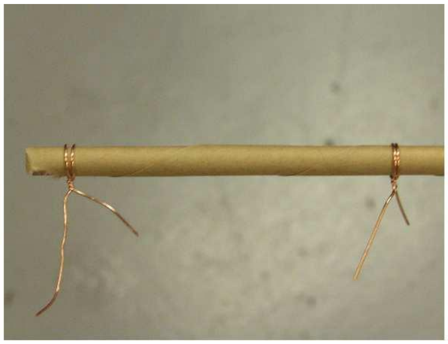
Section 6.2.6, Part 2



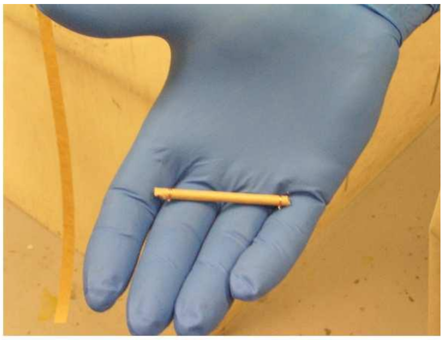
Section 6.2.6, Part 3



Section 6.2.7



Section 6.2.8



Section 6.2.9

7. Procedure

7.1 Place the aluminum block with the prepared vials into the oven at 140 ± 2°C.

7.2 Remove the aluminum block with vials after heating for 96 h (4 days) ± 40 minutes at 140 ± 2°C. Allow the block and vials to cool before processing. (Note: More pronounced results can be obtained if the samples are allowed to age for 6 at 140 ± 2°C instead of 4 days).

7.3 Decrimp the vial cap from the vial and decant the oil. Remove the paper wrapped copper rod from the vial. Remove the wire securing the paper wrapped copper rod ends.

7.4 Remove the paper from the copper rod and soak or rinse the paper and copper in pentane until the oil is removed. Three washes of pentane have proven satisfactory in removing the oil.

7.5 Mount the copper and the paper with the inside facing out so that it can be viewed.

7.6 To inspect the copper rod, hold the copper rod in such a manner that light reflected from it at an angle of approximately 45° will be observed.

7.7 To inspect the paper, hold the paper in such a manner that light reflected from it at an angle of approximately 30 to 45° will be observed.

8. Interpretation of Results

8.1 Classify the copper rod as having corrosive or non-corrosive in accordance with Table 1. The cut ends of the copper rod are to be considered as well during the inspection and classification. Classification of corrosive or non-corrosive may be aided through the use of ASTM Copper Strip Corrosion Standards as referenced in ASTM Method D 130.

8.2 The paper is inspected for the presence of a deposit. Examine both the outside and inside surfaces for deposits. A majority of the deposits will form on the inside surface and because of the way that the copper rod is wrapped most of the deposits will be in the center of the paper running lengthwise (see Figure 1). The result "deposition" whether heavy, moderate or light means that the interaction of the copper and oil with the paper insulation over the duration of the test resulted in an obvious deposit of copper sulfide, copper, or oil/paper degradation byproducts onto or in the paper insulation. Many oils tend to form some sort of deposit. Classify as follows (examples are provided in Figure 1):

8.2.1 Heavy Metallic-shiny deposits covering most of the surface, can consist of a multiple of colors including silvers, purples, greens, reds, etc. This is deemed corrosive.

8.2.2 Medium Metallic-same type of deposits like as described in Section 8.2.1 but covering a half or less or the insulation exposed to the copper. This is deemed corrosive.

8.2.3 Light Metallic-same type of deposits like as described in Section 8.2.1 but covering a quarter or less or the insulation exposed to the copper. This is deemed corrosive.

8.2.4 Heavy Dull-very dull matted deposits covering most of the surface, can consist of a multiple of colors including blacks, grays and greens. Dark brown/tan deposits are usually from oxidation of the paper and are not classified as deposits. This is deemed non-corrosive.

8.2.5 Medium Dull-same type of deposits like as described in Section 8.2.4 but covering a half or less or the insulation exposed to the copper. This is deemed non-corrosive.

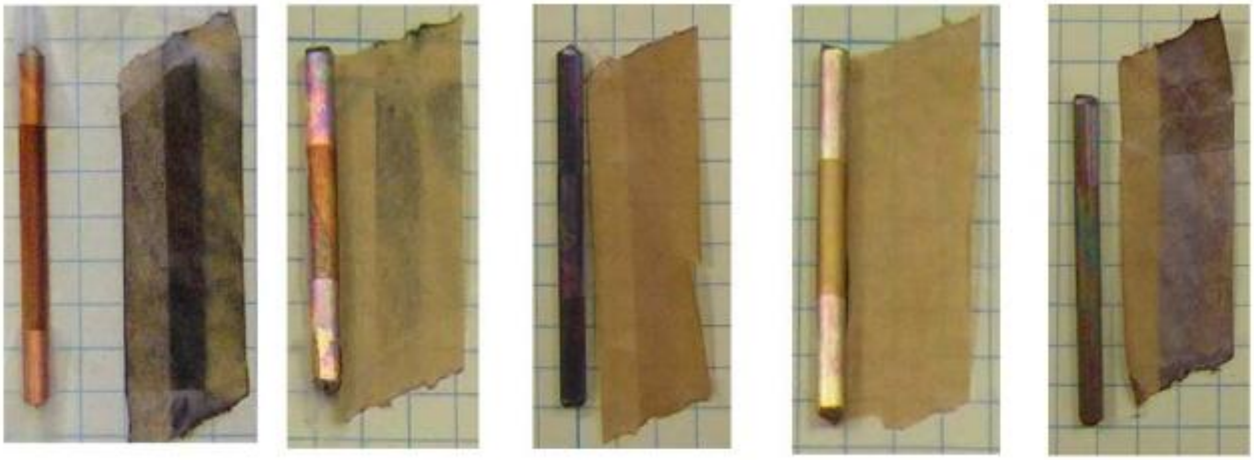
8.2.6 Light Dull-same type of deposits like as described in Section 8.2.4 but covering a quarter or less or the insulation exposed to the copper. This is deemed non-corrosive.

8.2.7 No Deposits-paper that has remained unblemished during the aging of the test specimen. Just a slight darkening of the paper or where oxidation of the paper is clearly visible would also be classified as having no deposits. This is deemed non-corrosive.

8.3 Confirmation tests can be used to aid in determining the type of deposit that is present when the coloration is not clear or difficult to determine (refer to Appendix X2).

TABLE 1 Copper Strip Classifications

Classification	Description
Non-corrosive	Orange, red, lavender, multicolored with lavender blue or silver, or both, overlaid on claret red, silvery, brassy or gold, magenta overcast on brassy strip, multicolored with red and green showing (peacock) but no gray
Corrosive	Transparent black, dark gray, graphite or lusterless black, glossy or jet black, any degree of flaking



Copper Non-Corrosive 2a **Paper** Heavy Dull

Copper Non-Corrosive 3b **Paper** Medium Dull

Copper Corrosive 4b **Paper** No Deposit

Copper Non-Corrosive 2e **Paper** No Deposit

Copper Non-Corrosive 2c **Paper** Heavy Metallic

FIGURE 1
EXAMPLES

9. Report

9.1 Report the following information:

9.2 Sample Identification,

9.3 Air Ingress Specimen

9.3.1 Identify the copper rod as “Corrosive” or “Non-corrosive” according to Table 1.

9.3.2 Identify copper rod as to the tarnish level according to ASTM D 130

9.3.3 Identify paper surface as to the type of deposit listed in Section 8.2.1 through and including 8.2.7 and list as corrosive or non-corrosive.

9.4 Sealed Test Specimen

9.4.1 Identify the copper rod as “Corrosive” or “Non-corrosive” according to Table 1.

9.4.2 Identify copper rod as to the tarnish level according to ASTM D 130

9.4.3 Identify paper surface as to the type of deposit listed in Section 8.2.1 through and including 8.2.7 and list as corrosive or non-corrosive.

9.5 If any of the copper rods or deposits on the paper are considered corrosive the oil is considered corrosive and fails the test. The oil should be reported as corrosive. If none of the copper rods or deposits are deemed to be corrosive the oil should be reported as non-corrosive

X1. Appendix

X1.1 A diagram of the aluminum block is shown in Figure 2. Sizes are approximate as the diameters of headspace vials fluctuate from manufacturer to manufacturer.

X1.2 Make holes deep enough so that the shoulder of the headspace vial is within 5mm of the edge of the shoulder. It does not matter if the bottom of the hole is flat or conical.

X1.3 The diameter of the holes should be just slightly larger than the vials being placed into them as heating and cooling of both the aluminum block and vials could cause them to break.

X1.4 The weight of the aluminum block makes it cumbersome to move and lift. Attaching a handle on one or both ends aids in transporting and lifting the block.

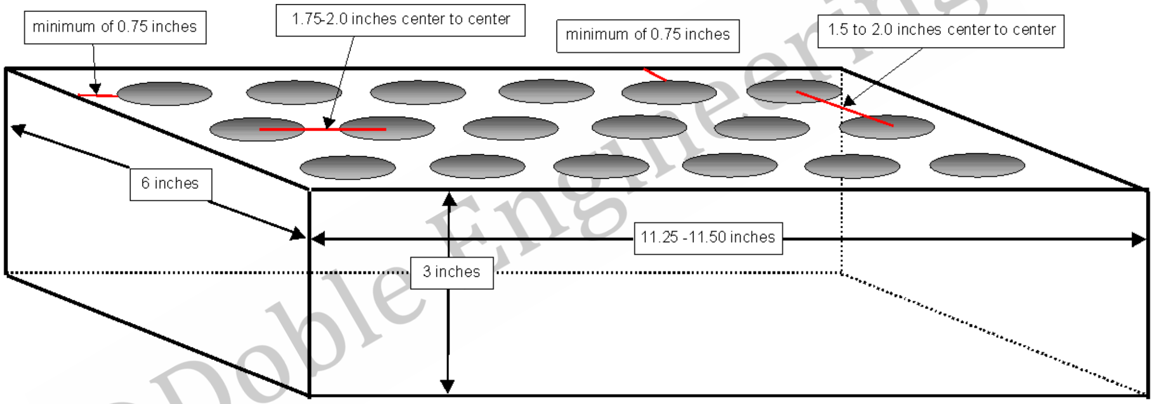


FIGURE 2

X2. Appendix

X2. Various confirmatory tests can be used to determine the type of deposit on the paper.

X2.1 *Dielectric Breakdown Voltage and Dielectric Strength of Solid Electrical Insulating Materials at Commercial Power Frequencies,* ASTM D 149, Method A with the following modifications– Dry and oil impregnated the paper according to ASTM D 2413. Fold the paper in half so that the inside surfaces face each other. Conduct test using 0.25 inch diameter electrodes in oil. In most cases only one breakdown is usually possible as opposed to the recommended five. Report the results in total voltage or volts/mil.

X2.1.1 For the maximum breakdown voltage obtained, values greater than 5000 volts would be considered acceptable. Values of 3000-4000 are marginal and values below 3000 volts would be considered poor or samples having deposits that adversely effect the insulating condition of the paper.

X2.2.2 For the maximum breakdown voltage obtained, values greater than 1300 volts/mil would be considered acceptable. Values of 601-1299 volts/mil are marginal and values below 600 volts/mil would be considered poor or samples having deposits that adversely effect the insulating condition of the paper.

X2.2 Scanning electron microscopy (SEM) – Energy dispersive X-ray (EDX) analysis are two separate tests conducted at the same time. EDX is a technique in which an electron beam of the scanning electron microscope enters the bulk of a sample producing a x-ray emittance. The x-ray peak positions, along the energy scale, identifies the elements present in the sample and can provide the percentage concentrations of each of these elements thus providing an elemental breakdown of the material or particles. SEM is an analysis in which a beam of electron, a few hundred angstroms in diameter, systematically sweeps over the specimen. The intensity of secondary electrons generated at the point of impact on the specimen surface is measured, and the resulting signal fed into a cathode-ray-tube display which is scanned in synchronism with the scanning of the specimen to produce a picture.

X2.2.1 Soak or rinse the paper in pentane until all the oil is gone. Leftover hydrocarbon residue will compromise the analysis.

X2.2.2 Locate the area on the paper that requires analysis, excise it and mount it to an SEM/EDX stub.

X2.2.3 Coat the prepared test specimen with evaporated graphite to improve imaging resolution and stability

X2.2.4 Conduct the SEM/EDX analysis on the prepared specimen. It is very difficult to scan a whole specimen so several spots should be selected prior to analysis. In paper test specimens where there is obvious and substantial metallic deposition, then only a single analysis may be required to confirm the results. Where questionable visual results are obtained, then 3 to 5 areas should be analyzed to obtain an overall confidence of the contamination level

X2.2.5 Record the weight and/or atomic percentages of the elements found. Depending on the age of the SEM/EDX equipment and the software, oxygen and carbon may be detected or it may be possible to subtract out the contributions of those elements. Use Tables 2 and 3 below for guidance in determining if copper sulfide is present and significantly above background.

Table 2: Use of Weight Percentages to Determine Presence of Copper Sulfide

Analysis Type	**Copper**	**Sulfur**	**Copper/Sulfur Ratio**	**Average Cu/S Ratio**
Oxygen and Carbon contributions are able to subtracted out (or) Equipment and/or software cannot detect oxygen & carbon	73.1…85.0%	14.5…18.5%	4.3…5.6	4.8:1
With the oxygen and carbon component present	11.5…50.5%	1.5…8.0%	5.6…9.2	6.8:1
Notes: 1). The copper percentage must be above 73% when the oxygen and carbon removed in order to be considered. 2). The copper percentage must be above 10% when oxygen and carbon is part of the total contribution in order to be considered.				

Table 3: Use of Atomic Percentages to Determine Presence of Copper Sulfide

Analysis Type	**Copper**	**Sulfur**	**Copper/Sulfur Ratio**	**Average Cu/S Ratio**
Oxygen and Carbon contributions are able to subtracted out (or) Equipment and/or software cannot detect oxygen & carbon	75.5…75.5%	21.4…31.7%	1.8…3.5	2.4:1
With the oxygen and carbon component present	2.6…21.5%	0.9…5.4%	2.3…4.2	3.2:1