THE ROLE OF CORROSIVE SULFUR IN TRANSFORMERS AND TRANSFORMER OIL

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INTRODUCTION

Corrosive sulfur and the effect that it has in transformer systems can be significant. The extent of the corrosion damage caused by sulfur, if left unchecked, can be so severe as to cause failure of the apparatus. The problems with corrosive sulfur have been recognized for quite some time. As early as 1948, F.M. Clark and E.L. Raab [1] issued a report on the subject for method development within what is known now as ASTM Committee D 27 and eventually became ASTM Method D 1275. Sulfur is found in many materials of transformer construction including the copper, paper insulation, gaskets and oil. Not all sulfur is considered corrosive but the tendency to operate transformers at substantially higher temperatures can aggravate an already present corrosive sulfur condition or convert stable compounds into reactive ones that will cause damage.

PRESENCE OF SULFUR IN MINERAL OIL

There are different types of sulfur compounds found in refined transformer oil but not all types are considered to be corrosive or reactive. Elemental sulfur and sulfur compounds in concentrations up to 20% [2] are present in the crude oil used to make transformer oil. There are five basic groups of sulfur and sulfur compounds found in crude oil (see Table 1) [2].

TABLE 1
Sulfur and Sulfur Compounds Found in Crude Oil

GROUP	CHEMICAL FORMULA	REACTIVITY
Elemental (Free) Sulfur	S	Very Reactive
Mercaptans (thiols)	R-SH	Very Reactive
Sulfides (thio-ethers)	$R\text{-}S\text{-}R_1$	Reactive
Disulfides	R-S•S-R	Stable
Thiophenes	Five-membered ring containing sulfur	Very Stable

R=paraffin with straight or branched chain hydrocarbon or cyclic hydrocarbon

Sulfur is commonly found in crude oil sources as it comprises almost 0.05% of the earth's crust. As shown in Table 1, elemental sulfur and the sulfur-containing mercaptans are very reactive followed by sulfides. Reactive sulfur is mainly in the form of organic sulfur compounds like R-SH, where the sulfur is attached at the end of an organic molecule. When the molecule is more complex, for instance when the sulfur is surrounded or contained within the molecule then the sulfur compounds are more stable and less reactive, like in R-S•S-R. Thiophenes are the most stable of all these sulfur compounds.

Some sulfur compounds can actually aid in the oxidation stability of the transformer oil and may also act as metal passivators and deactivators reducing the catalytic effect on oil oxidation in transformers. The goal of the refining process is to either remove or convert many of the corrosive and reactive sulfur species (i.e. elemental sulfur, mercaptans, and sulfides) to more stable compounds such as thiophenes in an unsaturated ring and disulfides in a saturated form. The steps in the refining process that aid in this effort are atmospheric distillation at various temperatures, vacuum distillation, catalytic reaction, and hydro-treating and hydro-generation [2,3]. It should be recognized that the refining process is not always totally successful as incomplete refining may leave small quantities of mercaptans behind or the hydrogenation process may produce elemental sulfur as opposed to hydrogen sulfide.

After refining, there is some sulfur left but the total sulfur (comprised of the five groups listed above) remaining in new oil product is expected to be from 0.02 % to 1% [2,3]. This information was slightly dated so the Doble Materials Laboratory analyzed several samples from Doble annual Survey 93 and found that most oils had a very low total sulfur content as shown in Table 2.

TABLE 2
Total Sulfur Content is Several Survey 93 Oils

Oil	Sulfur Content
Calumet Caltran 60-08	0.006%
Cross Oil CrossTran 106	0.012%
Ergon Hyvolt II	0.006%
San Joaquin Hytrans 61	<0.001%
Shell Diala AX from Deer Park	0.073%

WHAT IS CORROSIVE SULFUR?

Corrosive sulfur species are defined as all organic sulfur compounds that will react with mercury to form sulfides, such as mercaptans. Elemental (free) sulfur is very reactive and will react to form corrosive acids. It has been suggested that low elemental sulfur levels (low ppm range) can cause a corrosive condition [4]. It has recently been suggested that the definition of corrosive sulfur be narrowed to apply only to elemental sulfur whereas those organo-sulfur compounds that react to cause a corrosive condition be termed reactive sulfur.

REACTIONS OF CORROSIVE AND REACTIVE SULFUR

Corrosive and reactive sulfur compounds can react on contact with copper and other metals. Copper is, by far, the least resistant metal to a sulfur attack. Effects of elemental sulfur are even more problematic as its ability to combine with copper does not require heat to promote the reaction. In oxygen deficient environments such as those found in sealed, gas blanketed and sealed conservator transformers, corrosive and reactive sulfur species combine with copper, aluminum, and other metals to form copper or cuprous sulfide (Cu_2S), aluminum sulfide (Al_2S_3) and other inorganic sulfides. Copper sulfide is black, gray, green, blue, or violet in color and is sometimes confused with carbon. Aluminum sulfide is a yellowish-gray material that can become very gray in the presence of oxygen and water.

In the presence of an oxygen environment such as that available in sealed transformers that have a significant leak, free breathing transformers, free breathing conservator transformers, and other free breathing apparatus such as OCBs and LTCs, different types of compounds are formed from the reaction of sulfur with metals. Oxygen can also become available from the copper itself. The copper used for the windings is usually CDA-110 (UNS-C11000) material for ETP copper which is termed electrolytic tough pitch. This specification has a minimum copper purity requirement of 99.90% and it is not considered an oxygen free material (<5 ppm). There is not an oxygen specification for CDA-110 but it is usually contains about 500 ppm of oxygen or less. Copper winding samples that the Doble Materials Laboratory has tested contained around 200-250 ppm of oxygen. Different grades of copper can contain much higher amounts of oxygen that is then available for use in a reaction with sulfur. Therefore, the manufacturer of the transformer must be careful in selecting the correct grade of material for construction. Reactions involving oxygen, sulfur, copper, aluminum, or other metals can produce copper or cuprous sulfite (Cu_2SO_3), copper sulfate ($CuSO_4$), aluminum sulfate [$Al_2(SO_4)_3$], and other inorganic sulfates. Copper sulfite is usually white to pale yellow in color whereas copper sulfate is white or pale brown in color and aluminum sulfate is a white material.

NONCORROSIVE TO CORROSIVE

One of the major questions is if noncorrosive sulfur species can be converted to corrosive and reactive species in a transformer. Experience has shown that non-corrosive sulfur can become corrosive after being exposed to elevated temperatures on hot metal surfaces and thus produce metal sulfides. This attack would corrode the metal surfaces. To make matters worse, the corrosion material could detach and become nuclei for discharge and gas inception [3]. This may not be of concern with oils with low sulfur contents that pass the corrosive sulfur test as the quantity of corrosive sulfur compounds produced may not be sufficient enough to cause extensive damage.

The published literature does not detail if arcing in a transformer can change stable sulfur species into reactive or corrosive forms. The Doble Materials Laboratory performed experiments in which a voltage of 25 kV was applied to sustain an arc through Cross Oil CrossTrans 106 transformer oil in a test cell equipped with a needle to sphere with a 0.1 inch gap. The CrossTrans 106 was found to be noncorrosive prior to testing. The arcing produced the following gases:

TABLE 3
Combustible Gases Produced from Arcing in CrossTrans 106

Gas	Concentration
Hydrogen	2370 ppm
Methane	255 ppm
Carbon monoxide	32 ppm
Ethane	38 ppm
Ethylene	496 ppm
Acetylene	4375 ppm

The oil was tested for total sulfur, elemental sulfur and organo-sulfur species before and after the experiment was conducted. Tables 4, 5 and 6 document this information.

TABLE 4
Total Sulfur Content of CrossTrans 106

Before Arcing Experiment	0.0118%
After Arcing Experiment	0.0117%

TABLE 5
Elemental Sulfur Content of CrossTrans 106

Before Arcing Experiment	<1 ppm
After Arcing Experiment	<1 ppm

TABLE 6
Organo-Sulfur Content of CrossTrans 106

COMPOUND	Before Arcing	After Arcing
hydrogen sulfide	<1 ppm	<1 ppm
sulfur dioxide	<1 ppm	<1 ppm
carbonyl sulfide	<1 ppm	<1 ppm
methyl mercaptan	<1 ppm	<1 ppm
ethyl mercaptan	<1 ppm	<1 ppm
methyl sulfide	<1 ppm	<1 ppm
carbon disulfide	<1 ppm	<1 ppm
isopropyl mercaptan	<1 ppm	<1 ppm
ethylene sulfide	<1 ppm	<1 ppm
tert-butyl mercaptan	<1 ppm	<1 ppm
n-propyl mercaptan	<1 ppm	<1 ppm
ethyl methyl sulfide	<1 ppm	<1 ppm
thiophene	<1 ppm	<1 ppm
sec-butyl mercaptan	<1 ppm	<1 ppm
isobutyl mercaptan	<1 ppm	<1 ppm
ethyl sulfide	<1 ppm	<1 ppm
n-butyl mercaptan	<1 ppm	<1 ppm
methyl disulfide	<1 ppm	<1 ppm
2-methyl thiophene	<1 ppm	<1 ppm
3-methyl thiophene	<1 ppm	<1 ppm
tetra-hydro thiophene	<1 ppm	<1 ppm
ethyl methyl disulfide	<1 ppm	<1 ppm
2-ethyl thiophene	<1 ppm	<1 ppm
2,5-dimethyl thiophene	<1 ppm	<1 ppm
3-ethyl thiophene	<1 ppm	<1 ppm
2,4 & 2,3-dimethly thiophene	<1 ppm	<1 ppm
3,4-dimethyl thiophene	<1 ppm	<1 ppm
methyl ethyl thiophenes	<1 ppm	<1 ppm
trimethyl thiophenes	<1 ppm	<1 ppm
tetramethyl thiophenes	<1 ppm	<1 ppm
benzothiophene	<1 ppm	<1 ppm
methyl benzothiophenes	<1 ppm	<1 ppm
dimethyl benzothiophenes	<1 ppm	<1 ppm
trimethyl benzothiophenes	<1 ppm	<1 ppm
tetra-methyl benzothiophenes	<1 ppm	<1 ppm
dibenzothiophene	<1 ppm	2 ppm
methyl dibenzothiophenes	11 ppm	19 ppm
dimethyl dibenzothiophenes	46 ppm	47 ppm
trimethyl dibenzothiophenes	54 ppm	59 ppm
tetra-methyl dibenzothiophenes	17 ppm	26 ppm
Unidentified volatile sulfur	<1 ppm	11 ppm
Total	128 ppm	147 ppm

The arcing did not reduce the total amount of sulfur left in the oil nor did it convert any of the sulfur compounds already present into free sulfur. However, conversion of some of the thiophene compounds did occur (see Table 6). The presence of sulfates and sulfites cannot be determined by this method and it may be that those were the compounds that were converted. This may explain the differences between the before and after test results. What is of significant interest is the amount of unidentified volatile sulfur compounds that were created through the arcing process. No mercaptans or sulfides (corrosive or reactive sulfur) were formed. The lack of these sulfur species may be a result of the energy applied through arcing that could have been so severe that any reactive or corrosive species that were produced were instantaneously degraded and thus none remain.

SOURCES OF SULFUR IN TRANFORMER SYSTEMS

Oil is not the only material that contains sulfur. Sulfur compounds are also present in the gaskets, some water-based glues, copper and paper insulation used in the manufacture of transformers. Sulfur can also be introduced into the transformer through accidental means such as through the use of incompatible hoses.

It is generally accepted that older gaskets used in transformer applications were made from cork, cork/glyptal, corkprene and then in more recent years, the most oil compatible gaskets have been nitrile rubbers such as BUNA-N and a fluoroelastomer such as VITON®. Properly made nitrile rubbers (butadiene acrylonitrile) and fluoroelastomers (fluorinated hydrocarbon) are excellent gaskets for use in transformers. In the manufacture of these materials, sulfur is used in the curing process when the formulations are being developed into a hardened material. The curing process is supposed to eliminate all sulfur from the finished product. Most gasket manufacturers assume that the sulfur is eliminated after the curing process. In some cases, the concentration of sulfur contained in the final gasket product is not monitored. Doble Engineering performed scanning electron microscopy/energy dispersive x-ray analysis (SEM/EDX) analysis on numerous gaskets taken from recently manufactured transformers. Each gasket was prepared for analysis by cleaning the outside surface with a sulfur-free hydrocarbon solvent. The gasket was then cut lengthwise to reveal the inside surface. The outside and inside surfaces of each gasket were coated with evaporated graphite. The samples were then subjected to SEM/EDX analysis 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, identify 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. Results from two gaskets are shown in Tables 7 and 8.

TABLE 7
Elemental (Inorganic) Composition of a O-ring Radiator Gasket

ELEMENT	Outside Surface	Inside Surface
Silicon	40.0%	10.6%
Zinc	27.2%	41.4%
Sulfur	21.5%	41.0%
Titanium	5.9%	0.0%
Calcium	5.4%	6.1%
Aluminum	0.0%	1.0%

TABLE 8
Elemental (Inorganic) Composition of a Butterfly Valve Flat Gasket

ELEMENT	Outside Surface	Inside Surface
Silicon	47.7%	44.8%
Aluminum	24.3%	28.7%
Zinc	11.9%	11.3%
Sulfur	10.3%	10.7%
Copper	2.0%	0.0%
Calcium	1.4%	1.4%
Titanium	1.4%	1.5%
Iron	1.1%	1.7%

The inside of the O-ring gasket had a slightly elevated background level which indicates that there is some organic component as well as the elemental component. Both gaskets contained a large amount of sulfur especially the O-ring gasket. The SEM/EDX analysis was performed on the inside surface of the gasket as well to distinguish between the outside surface possibly being contaminated with corrosive sulfur from the oil. It is clear that sulfur is a component of both original gaskets. The original formulations for a nitrile rubber, fluoroelastomer or a silicone rubber, which is a polydimethylsiloxane, do not contain any sulfur.

In discussions with elastomer manufacturers it was found that very few if any manufacturers, (except for E.I. Dupont) were performing any chemical testing on the finished product to determine what amount of sulfur remained if any. There also does not appear to be any standard on what percentage of sulfur should remain in the final product. It then becomes obvious that the onus is on the final user of the material to specify a sulfur-free or low-sulfur material for use or to test it prior to use.

In light of this information, additional SEM/EDX analysis was performed on gasket material that was available in the Doble Materials Laboratory. One sample was a fluoroelastomer and another was a nitrile rubber produced by Parker. The results are shown in Tables 9 and 10.

TABLE 9
Elemental Composition of a Fluoroelastomer Gasket

ELEMENT	Outside Surface	Inside Surface
Fluorine	High	Very High
Organic Component	High	Very High
Calcium	68.8%*	74.0%*
Magnesium	10.6%*	24.7%*
Chlorine	3.1%*	1.3%*
Silicon	4.0%*	0.0%
Phosphorous	4.0%*	0.0%
Aluminum	3.6%*	0.0%
Sulfur	3.3%*	0.0%
Potassium	2.7%*	0.0%

*Note: SEM/EDX analysis cannot quantity elements such as fluorine, nitrogen, oxygen, carbon, hydrogen, and boron but can sometimes give a qualitative indication of the amount in high enough concentrations. In this particular case, the fluorine and organic component of the inside surface probably comprised greater than 90% of the material. Because of this, the calcium, magnesium and chlorine would be components of the remaining 10% such that it would give you overall concentrations of approximately 7.4% calcium, 2.5% magnesium and 0.1% chlorine. This would also be true for the outside of the gasket.

TABLE 10
Elemental Composition of a Parker Nitrile Gasket

ELEMENT	Outside Surface	Inside Surface
Organic Component	High	High
Sulfur	49.2%*	54.5%*
Zinc	35.8%*	36.9%*
Aluminum	7.9%*	4.2%*
Silicon	7.2%*	4.5%*

*Note: Same note as above for Table 9 but the majority of the composition is organic with no fluorine.

As shown in the two tables above, the fluoroelastomer shows no sulfur on the inside surface and very little on the outside suggesting that material was cured correctly. The opposite is true of the Parker nitrile material which shows an extremely high sulfur content on both surfaces suggesting that the sulfur was not removed after the curing process.

Water-based glues, used to secure the paper insulation during manufacture, often contain sulfur compounds. There has been at least one known instance in which the glue used in the manufacture of the windings has contributed to a corrosive sulfur condition.

Most coppers used in manufacturing transformer windings contain some impurities and sulfur happens to be one, along with silver, arsenic, phosphorous, tellurium and oxygen. The amount of sulfur that is allowed in most of the electrical grades of copper is 15 ppm or less. In the analysis performed at the Doble Materials Laboratory on copper samples from windings, the sulfur contents were very low at 5 ppm or less. However, there still has to be care taken in the selection of materials used in construction so that copper with a high sulfur content is not used.

The pulping process for electrical Kraft paper converts the wood chips to cellulose by removing the majority of lignin (95-98.5%) and other impurities [5]. There are two basic processes. The sulfite process is considered an acidic process and uses sulfur dioxide, sulfuric acid and calcium bisulfite. The main process used today and the one that is used to produce electrical grade Kraft papers is the sulfate process which is also called alkaline pulping. Sodium hydroxide and sodium sulfide is used in what is termed the cooking process. The cooking process under conditions of heat, pressure and chemicals (pulping liquors) removes the lignin and impurities from the wood chips in order that only cellulose remains. The pulping liquor is removed and recycled for use again and the remaining cellulose pulp is washed several times to remove as much as the pulping liquor as possible from the cellulose pulp. The Kraft process is slightly different in that the same chemicals are used but the pulp is intentionally undercooked and results in the darker color of the paper as well as exceptional mechanical strength. The pulp fibers in the Kraft process do absorb some of the sulfur compounds that cannot be removed via the washing/rinsing process [5]. The Doble Materials Laboratory performed analysis to determine how much total sulfur remains in the finished paper products. The first analysis performed was SEM/EDX analysis of new Kraft and thermally-upgraded (TU) Kraft from United States manufacturers. These results are listed in Table 11 and are for the surface of the paper only.

TABLE 11
Surface Composition of Kraft and TU Kraft

ELEMENT	KRAFT	TU-KRAFT
Organic Component	High	High
Calcium	71%	50%
Sulfur	7%	21%
Silicon	21%	29%

*Note: Although the elemental concentrations seem very high, they are really just a fraction of a percent as most of the material is organic material (cellulose).

In addition, several different samples of Kraft paper insulation were analyzed for total sulfur and total sulfate content. The results are present in Table 12.

TABLE 12
Sulfur Composition in Various Electrical Papers

PAPER	Total Sulfur Content*	Total Sulfate Content*
Kraft Paper-1	700 ppm	205 ppm
Kraft Paper-2	300 ppm	<7.5 ppm
TU-Kraft	700 ppm	158 ppm
Kraft Crepe Paper-1	600 ppm	93 ppm
Kraft Crepe Paper-2	500 ppm	30 ppm

*Total sulfur analysis was performed by ASTM Method D 129 and total sulfate analysis was performed by EPA Method 300.0

As shown in Table 12, the amount of sulfur varies between various manufacturers of electrical paper and sometimes considerably. The amount of sulfur present is fairly significant in most of the samples. The amount of reactive or corrosive sulfur in relation to the total is unknown although it is assumed that the amount of sulfates in the sample is at least the minimum amount.

Accidental contamination of the transformer oil with corrosive and reactive sulfur compounds can occur by use of incompatible materials or contaminated processing equipment to transfer oil. For example, hoses that are made from natural rubber or gasoline hoses both contain high amounts of sulfur that are easily transferable to the oil that is being pumped through them. Extra care must be exercised in the selection of hoses so that no incompatibility exists. Oil processing equipment runs the risk of being contaminated from processing a transformer with corrosive and reactive sulfur to another transformer that does not. The best safeguard is to check the remaining oil left in the processing equipment prior to its next use.

As described above, several materials in the transformer will contain sulfur such as the copper, paper and oil. In some cases, the sulfur species in question are stable or are so tightly bound in the material that they would not be available for reactions. In other cases some of the sulfur compounds are corrosive or reactive. In these cases, appropriate material compatibility testing should screen out these materials before they are used in transformer construction.

EFFECTS OF CORROSIVE/REACTIVE SULFUR

Corrosion of the metal surfaces especially exposed copper surfaces is one of the primary reactions of a corrosive/reactive sulfur condition. Figure 1 shows how exposed metal surfaces can be worm-holed by a corrosive/reactive sulfur attack. Figure 2 shows NLTC contacts that are overly contaminated with what appears to be a buildup of carbon but in reality is copper sulfide.

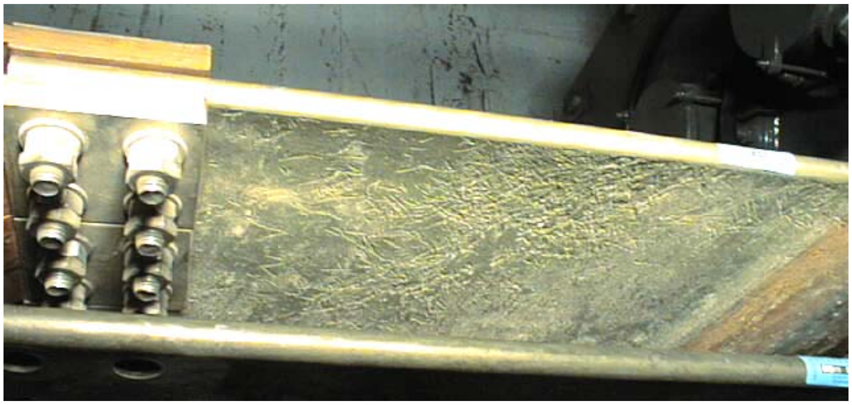


FIGURE 1
Corroded Bus Bar Surface

FIGURE 2
Copper Sulfide-Contaminated NLTC Contacts

The NLTC contacts shown in Figure 2 were discovered by accident. A maintenance function involving a power transformer led to the belief that a piece of hardware had fallen into the main tank of the transformer. A visual inspection was conducted through the manhole of the unit and the blackened NLTC contacts were visibly apparent. This caused the unit to be removed from the station, drained and inspected by entering through a manhole. After draining and entering the unit, personnel wiped the NLTC contacts with a cloth and discovered that the plating of the contacts was removed along with the black material. This of course caused concern and an investigation was initiated in which it was determined that copper sulfide, not carbon was the black shiny material found on the contacts. This type of corrosion, as shown in Figures 1 and 2, could easily lead to overheating and arcing of these components thus severely damaging or causing failure of the apparatus. The effects of a corrosive/reactive sulfur attack on a metal conductor do not always result in a black coating. In some cases, a silver coating or a silver discoloration of the copper conductor surface occurs as in Figure 3.

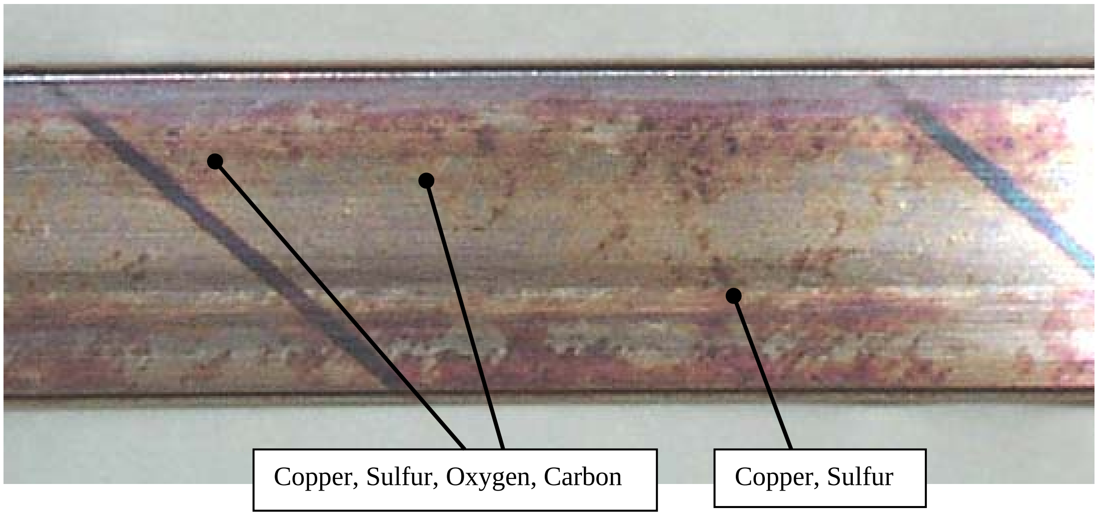


FIGURE 3
Copper Sulfide/Sulfate-Contaminated Copper Conductor

Metal is not the only surface that is affected by corrosive and reactive sulfur. Sulfur reactions with paper-wrapped conductors can cause some of the conductor, such as copper or aluminum, to be transferred to the surface of the paper. In some instances, the transfer can be extensive as shown in Figure 4.

Layer 1: Next to Conductor Side facing conductor	
Element	**Conc.**
Copper	78.4%
Sulfur	17.4%
Silicon	2.8%
Calcium	4.4%

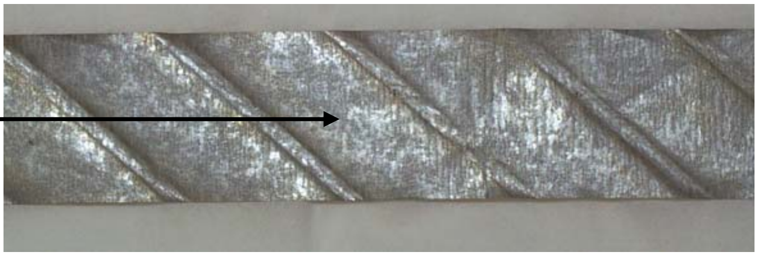


FIGURE 4
Copper Sulfide/Sulfate-Contaminated Conductor Insulation

The analysis on the paper surface shown in Figure 4 was performed by SEM/EDX as previously described. In analysis performed on paper, the SEM/EDX analysis usually indicates a very high organic content due to the cellulose composition. In this particular case (Figure 4), the copper-sulfur contamination that had been transferred to the paper insulation had been significant enough to mask out most of the organic component. In analyzing this paper, a closer examination of the surface was conducted and SEM micrographs were produced at a magnification of 200 times. Figure 5 is a SEM micrograph of uncontaminated Kraft paper and crepe paper.

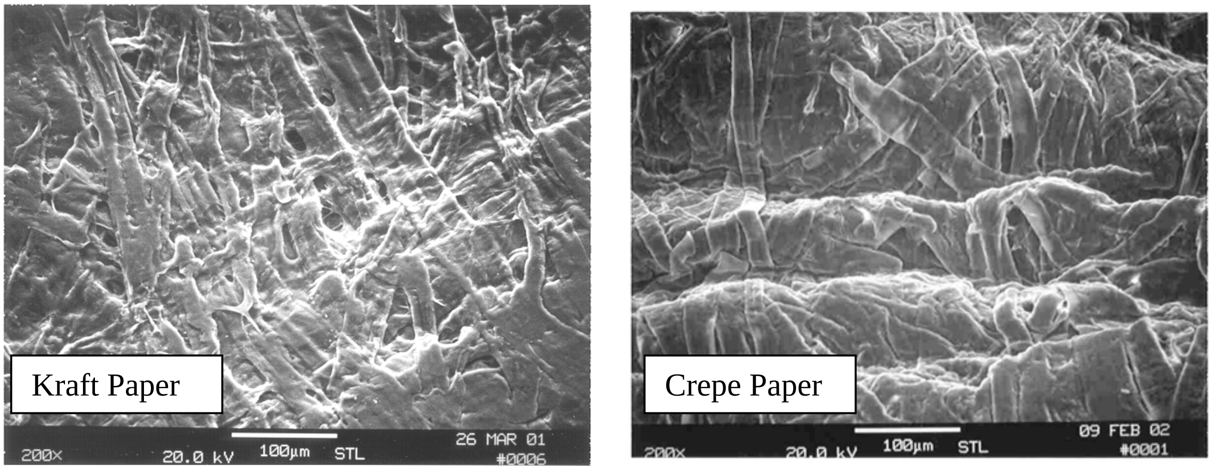


FIGURE 5
Uncontaminated Conductor Insulation

The individual paper fibers are clearly visible in both the Kraft and crepe papers in Figure 5 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 6.

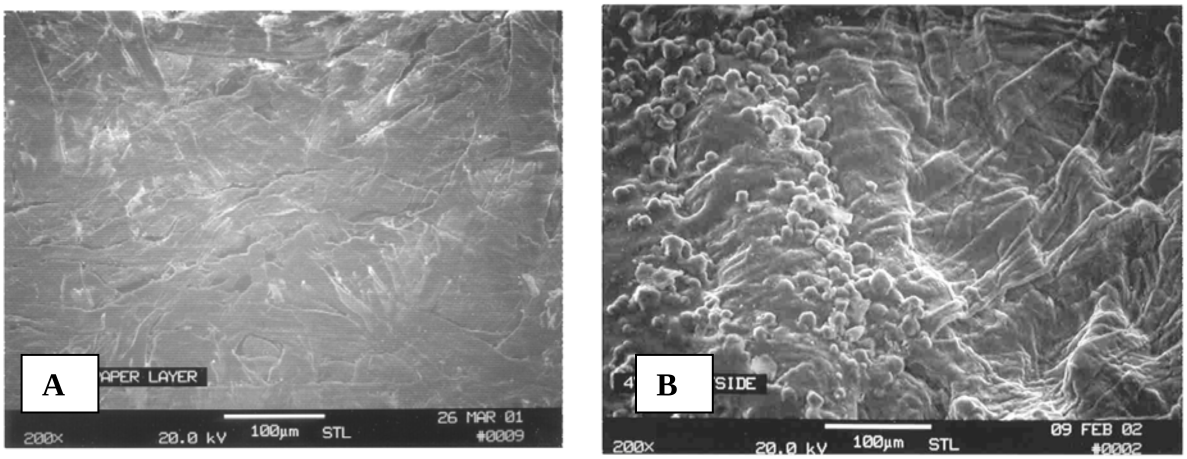


FIGURE 6
Contaminated Conductor Insulation

All the fiber surfaces and the gaps between the fibers are encrusted with a contaminating material in Figure 6A. The contamination present on the surface of the paper in Figure 6B has not yet progressed to the same point as in Figure 6A but there is significant contamination present and consists of mainly copper sulfides and sulfates. The small spherical structures in the left-hand portion of Figure 6B are composed mainly of copper and aluminum sulfides and sulfates.

In an effort to evaluate the effect that this type of contamination has on paper insulation, dielectric breakdown strength testing, by ASTM Method D 149, was performed on the three layers of insulation that surrounded the copper conductor. The first layer or the one closet to the conductor was the insulation shown in Figure 6A. The other two layers of paper insulation were also contaminated but not to the degree of the first layer. The results of this testing is shown in Figure 7.

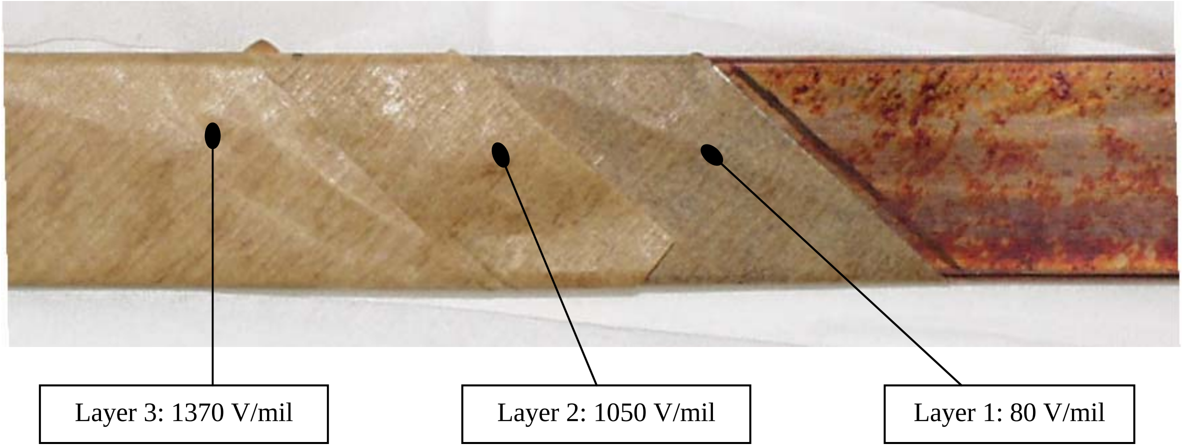


FIGURE 7
Dielectric Strength Testing of Contaminated Conductor Insulation

Layer 1, shown in Figure 7, had an extremely low dielectric strength at 80 volts/mil. As the contamination is reduced with each paper layer further out from the conductor, the dielectric strength increases significantly to almost as new condition (1800 volts/mil oil impregnated). Of significant interest is the fact that the mechanical strength was not impacted by the contamination as the DP values for all three layers ranged from 903 to 938. The silvery appearance of the paper in Figure 4 is due to the alteration of the sulfur-bearing compound due to exposure to higher temperatures, as copper sulfide is usually gray-black in appearance. This reaction of copper and sulfur created deposits on the first and second layers of paper on the same sample. Because of the deposition of the copper and sulfur, the first inside wrap became a poor insulator and instead was more conductive. When the corrosive sulfur contamination is this severe, a failure of the transformer is almost inevitable as in this case.

TESTING FOR SULFUR COMPOUNDS

Several tests are needed to identify and measure elemental sulfur and the numerous sulfur compounds found in oil samples or in solid materials used in transformers. Some methods will measure corrosive sulfur, total sulfur, elemental sulfur, inorganic sulfates and organo-sulfur compounds in oil. The most widely used in the electrical oil industry is ASTM D 1275, which is the Standard Test Method for Corrosive Sulfur in Electrical Insulating Oils [6]. In this test, 250 mLs of oil is added to a beaker with an abraded and polished copper strip. The oil is sparged with dry nitrogen for 1 minute, stoppered and aged for 19 hours at 140ºC. The coloration of the copper strip after the test is conducted, determines whether or not the oil is corrosive. This test is greatly affected by oxygen. If oxygen is present, then unstable sulfur compounds are reduced and will not react with the copper strip, so it is imperative that the test be conducted under the nitrogen conditions imposed by the method [1]. Similar test methods to the ASTM D 1275 are ISO Method 5662 and the German Method DIN 51353: Testing of Insulating Oils, Detection of Corrosive Sulfur, Silver Strip Method [7]. The German method uses silver instead of copper and is said to be more sensitive, and the reaction clearer. There is also a proposed new method within the IEC. The method is based on a potentiometric titration of 40 grams of oil dissolved in 60 mLs of propanol against a silver nitrate solution. The method however is insensitive to elemental sulfur whereas the other three methods listed above are.

Total sulfur can be detected by various methods. Two methods commonly used are ASTM methods D 3120 and D 2622. ASTM D 3120 involves the oxidative pyrolysis of the sample under argon with oxygen. This converts the sample to sulfur dioxide (SO_2) which is then titrated coulometrically. This method has a lower detection limit of 3 ppm (0.0003%), but a maximum detection limit of only 100 ppm (0.01%). ASTM D 2622 involves the use of wavelength dispersive X-Ray fluorescence spectrometry. In this method, the lower detection limit is 10 ppm (0.0010%) whereas the upper detection limit is greater then 100,000 ppm (10%). Elemental sulfur determination can be performed by method UOP-377, which is a Universal Oil Products Test Method for "Free Sulfur in Liquefied Petroleum Gases by Mercury Index Number". This method has a detection limit of 1 ppm.

Inorganic sulfates can be detected by ASTM Method D 878, which is the "Standard Test Method for Inorganic Chlorides and Sulfates in Insulating Oils." This is a qualitative method where a white precipitate is formed if there is a reaction with inorganic sulfates. The lower level of detection is 6 ppm. However, this method detects neither organic sulfates nor inorganic sulfides or sulfites.

Organo-sulfur speciation is performed by ASTM Method D 5623 and is the "Standard Test Method for Sulfur Compounds in Light Petroleum Liquids by Gas Chromatography and Sulfur Selective Detection". The concentration range of detection is from 0.1 to 100 ppm. This method only analyzes for organo-sulfur compounds and does not detect elemental sulfur, sulfates, sulfites nor inorganic sulfides.

In some cases it is very easy to determine if corrosive sulfur exists in an oil. However, determination of the specific element or compound is much more problematic and time consuming. It is not always necessary to know the compound, but other situations dictate that the possible source of the contamination be determined in order for the contamination to be remediated. The methods described above aid in that investigation.

EXPERIMENTS CONDUCTED AT THE DOBLE MATERIALS LABORATORY

Ever since the excellent presentation by Alberto Herreño Rocha on faults in 500-kV shunt reactors due to corrosive sulfur [8] at the 2001 Doble conference, the Doble Materials Laboratory has conducted numerous experiments involving the role of sulfur compounds in transformer oil and transformers. Besides the several investigations already detailed above, experiments involving gaskets, plating of the silver coating onto paper (refer to Section on "Effects of Corrosive Sulfur"), and processing of the oil to remove corrosive sulfur were conducted.

a. GASKET EXPERIMENTS

In the section entitled "Sources of Sulfur in Transformer Systems" it was shown that gaskets tested contained sulfur, zinc and silicon as well as other compounds. The purpose of this experiment was to determine if any of these materials would leach from their respective gaskets into the oil. The significance of test was that if sulfur had leached into the oil, it could cause a corrosive condition depending on the type of sulfur.

Each gasket was prepared for two experiments, one of short duration and one of long duration. Twenty (20) grams of each gasket were submerged into 800 mLs of Calumet Caltran 60-08 and further prepared according to ASTM Method D 3455. The first experiment involved aging both gaskets for 164 hours at 100°C. After aging for 164 hours, the oil that each gasket was immersed in was submitted for corrosive sulfur testing at both 140 and 150°C.

The second experiment involved the use of the same gasket material as in the first experiment, except that the temperature was increased to 115°C and the duration lengthened to 432 hours, (18 days). After aging for 432 hours, the oil from the test was submitted for corrosive sulfur testing at both 140 and 150°C. The results are presented in Tables 13.

TABLE 13

Results from Gasket Aging Experiments

Test	Results of O-ring Gasket	Results of Flat Gasket
Surface area of gasket exposed to oil	107.4 cm^2	105.7 cm^2
Weight of gasket used in test	20.4 grams	20.0 grams
Visual	No change in gasket, oil slightly yellowed	No change in gasket, oil yellowed more so than oil with the o-ring gasket
Weight Change	+0.2 grams	+0.3 grams
164 hours, Corrosive Sulfur at 140°C	Noncorrosive	Noncorrosive
164 hours, Corrosive Sulfur at 150°C	Noncorrosive	Noncorrosive
432 hours, Corrosive Sulfur at 140°C	Noncorrosive	Noncorrosive
432 hours, Corrosive Sulfur at 150°C	Noncorrosive	Noncorrosive
Interfacial Tension of the oil (432 Hrs), D 971	36 mN/m	34 mN/m
Neut. No. of the oil (432 Hrs), D 974	0.035 mg KOH/g	0.030 mg KOH/g
Power Factor of the oil at 25°C (432 Hrs), D 924	0.0199%	0.0145%

An ICP metals test was also performed on a control sample and each test oil to determine if any other material may have leached out during the testing. The results of this analysis are provided in Table 14.

TABLE 14
Elemental Results from Gasket Aging Experiments

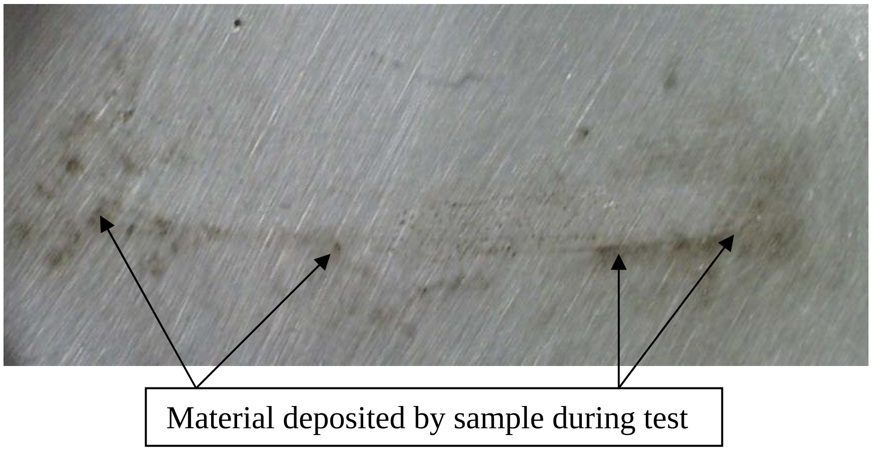
	Control Sample	O-Ring Cooler Gasket		Flat Gasket	
ELEMENT	Before TEST	After 164 hours	After 432 hours	After 164 hours	After 432 hours
Iron	<1 ppm	<1 ppm	<1 ppm	<1 ppm	<1 ppm
Chromium	<1 ppm	<1 ppm	<1 ppm	<1 ppm	<1 ppm
Lead	<1 ppm	<1 ppm	<1 ppm	<1 ppm	<1 ppm
Copper	<1 ppm	<1 ppm	<1 ppm	<1 ppm	<1 ppm
Tin	<1 ppm	<1 ppm	<1 ppm	<1 ppm	<1 ppm
Aluminum	<1 ppm	<1 ppm	<1 ppm	<1 ppm	<1 ppm
Nickel	<1 ppm	<1 ppm	<1 ppm	<1 ppm	<1 ppm
Silver	<1 ppm	<1 ppm	<1 ppm	<1 ppm	<1 ppm
Molybdenum	<1 ppm	<1 ppm	<1 ppm	<1 ppm	<1 ppm
Titanium	<1 ppm	<1 ppm	<1 ppm	<1 ppm	<1 ppm
Silicon	<1 ppm	<1 ppm	<1 ppm	<1 ppm	<1 ppm
Boron	<1 ppm	<1 ppm	<1 ppm	<1 ppm	<1 ppm
Sodium	<1 ppm	1 ppm	<1 ppm	<1 ppm	1 ppm
Magnesium	<1 ppm	<1 ppm	<1 ppm	<1 ppm	<1 ppm
Calcium	<1 ppm	<1 ppm	<1 ppm	<1 ppm	<1 ppm
Barium	<1 ppm	2 ppm	2 ppm	2 ppm	<1 ppm
Phosphorous	<1 ppm	<1 ppm	<1 ppm	<1 ppm	<1 ppm
Zinc	<1 ppm	49 ppm	96 ppm	13 ppm	5 ppm
Vanadium	<1 ppm	1 ppm	1 ppm	2 ppm	1 ppm

As shown in Table 14, both gaskets leached some barium, sodium, vanadium and a lot of zinc into the oil but no sulfur. Since these were not new gaskets, it is possible that any sulfur that could have leached out may have already done so while in service. The data in Table 13, demonstrates that the presence of the gasket in the oil during aging, caused discoloration of the oil. In both tests the oil with the flat gasket had yellowed more than the oil with the o-ring gasket. The neutralization number of the oil did increase and the IFT did decrease but this is not totally unexpected for a test of this duration. The power factor remained relatively low.

b. PLATING EXPERIMENTS

A theory has been presented that suggests that the silver coating found on the copper and paper samples shown in Figure 4 was produced from the plating of the sulfur in the oil to the copper and paper in the presence of a D.C. voltage. To test this theory, a Kraft paper wrapped conductor with seven layers of insulation was immersed in one liter of oil known to contain corrosive sulfur and a D.C. voltage was applied. A similarly wrapped conductor was prepared and immersed into one liter of an oil that had a very low sulfur content and no corrosive sulfur (San Joaquin Hytrans 61). The amount of copper conductor used per sample was 12.5 grams and the amount of paper used per sample was 0.7 grams. A control sample was also prepared in the same manner and immersed in oil but no voltage was applied.

A D.C. voltage of 5000 volts was applied continuously for 14 days. After the testing was completed the samples were removed for visual inspection and dielectric testing. The visual inspection of the paper samples did not indicate any discoloration between all three samples. The copper surface of the sample immersed in the corrosive-sulfur oil was slightly more discolored than the sample without corrosive sulfur present. This discoloration was found to be carbon deposits indicating localized overheating. Of more interest was the deposition of material from the corrosive-sulfur sample on the stainless steel surface on which the sample rested (see Figure 8).



Material deposited by sample during test

FIGURE 8
Material Deposited on Stainless Steel Platform During Test

Upon closer inspection the marks on the stainless steel surface resembled burning marks. The sample that was immersed in noncorrosive oil did not produce any deposits or marks on the stainless steel surface. The results from the dielectric testing of the paper performed in accordance to ASTM D 149 are provided in Table 15.

TABLE 15
Paper Dielectric Strength Test

Sample	Dielectric Strength
Paper Sample in Corrosive Oil	452 volts/mil
Paper Sample in Noncorrosive Oil	431 volts/mil
Control Sample	1567 volts/mil

As expected, the control sample had the highest dielectric strength. Unexpectedly however, the two paper samples tested under the conditions of D.C. voltage had nearly the same dielectric strength regardless of the type of oil they were immersed in. This phenomenon is not yet understood. Both samples did show an increase of the dielectric strength of the paper from the inside layer next to the conductor (lowest dielectric strength) to the outermost layer (highest dielectric strength).

The application of the D.C. voltage did have an effect on the dielectric strength of both paper samples tested. It has been postulated that a lightening strike on a transformer can temporarily charge the winding so that a D.C. voltage is present and superimposed with the AC voltage. This effectively turns the winding into a capacitor in which the paper and the oil insulation hold a charge. However, that phenomenon is short lived (a few seconds) as the D.C. voltage quickly dissipates due to losses in the solid and liquid insulation. In addition, plating by D.C. voltage does occur but it is a lengthy process as shown in this experiment in which a silver coating never formed on the paper insulation even after 14 days at 5000 volts D.C.

c. PROCESSING OIL TO REMOVE CORROSIVE SULFUR

Several methods were examined to see if they could be used to reduce the corrosive sulfur content in transformer oil. An oil that clearly failed the corrosive sulfur ASTM test D 1275 was used for the experiments. The oil was treated with Fuller's earth (clay) at a ratio of 30 grams of clay per liter of oil (0.25 pounds of clay: 1 gallon of oil) at two temperatures, 45 and 85°C. This type of treatment proved to be futile in that the treated oils failed the ASTM Test D 1275. Another type of process using a synthetically manufactured absorptive also proved to be unsuccessful in removing the corrosive sulfur. The last test involved the use of activated carbon. Three hundred milliliters of contaminated oil were processed through 128 grams of carbon activated at 120°C for 24 hours. The sample was then tested according to ASTM D 1275. The treated sample failed the test indicating that is was still corrosive.

Currently, the only successful way to remove corrosive sulfur from transformer oil is to remove it from the transformer and dispose of it. Adequate flushing of the transformer should be effected to remove or dilute any remaining contaminated oil in the system. If the oil has been present in the transformer system for some time then damage to the insulation or the metal surfaces may have already occurred and should be taken into consideration. However, removal and replacement of the contaminated oil may help to mitigate any future damage.

CONCLUSIONS

Sulfur and sulfur bearing compounds in transformer mineral oil can present a multi-faceted problem. Crude oils used to refine transformer oils can contain large amount of sulfur. The goal of the refining process is to remove as many sulfur compounds through various means and convert other reactive compounds into stable ones. There are basically five types of sulfur bearing compounds that can exist in transformer oil. Free (elemental) sulfur and linear and branched sulfur compounds, such as mercaptans and sulfides, are the most reactive and consequently cause the most damage. Disulfides are fairly stable and the thiophenes are the most stable and actually impart oxidation stability to the oil.

There are many internal and external sources of sulfur within a transformer besides the oil. Internal sources include the copper, paper, gaskets, glues, and possibly other materials. External sources usually include inadvertent contamination from incompatible materials such as oil transfer hoses.

Although the action of corrosive and reactive sulfur on copper can occur at ambient temperatures, it is theorized that higher temperatures either activates the conversion of relatively stable sulfur species to corrosive or reactive forms or allows reactions to occur between some sulfur compounds and metals. This process is also most likely time dependent and it may have taken several months or years to manifest. It is believed that elevated temperatures in localized areas is the main driver as certain areas in a transformer are seriously affected when other areas remained untouched.

The effects of corrosive/reactive sulfur not only adversely affect the conductor material and other metal surfaces but also can have drastic effects on insulating materials such as paper. Information presented in this paper clearly demonstrates that serious contamination due to sulfur-containing surfaces can drastically reduce the dielectric strength of the paper insulation while no or very little change has taken place in the mechanical strength of the paper as measured by DP.

Identifying the sources of sulfur contamination and being able to monitor concentrations of corrosive and reactive sulfur will help defect problem areas earlier. Therefore, a multi-faceted approach is employed in which different tests are used to provide complementary and meaningful information. Other than draining and flushing with new oil, a commercially-viable remedial process has not been developed which can remove corrosive and reactive sulfur species from the oil. Hopefully, a method for treating the contaminated oil can be developed and Doble is continuing this research.

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