

# Transformer Oil Corrosive Sulfur Problem and Solutions

by **Frank May**

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Transformer operation should be evaluated from three viewpoints: social, economic and environmental. First, transformers must be reliable to provide uninterrupted electrical power to clients. Second, transformer operation should not involve unforeseen expenses. Third, the transformer must run for as long as possible without generating waste products that require special disposal. One of the problems impacting all three of the above is corrosive sulfur and its compounds in insulation oil. As the name implies, it causes premature wear and corrosion and it can make the oil unusable.



The sulfur problem is not as cut and dried as that, however, since some sulfur compounds are known to have a positive effect on transformer oil performance, such as methyl phenyl sulfide and  $\alpha$ -naphthyl thiophane, which improve the oxidation stability of the insulation fluid. It is also known that non-corrosive substances may become such at elevated temperatures.

## The sources of sulfur in transformers

Transformer oil includes complex mixtures of hydrocarbons of various origins, sulfur compounds, a small amount of oxygen and nitrogen compounds, and trace metal organic substances. As far as sulfur is concerned, these compounds can enter the oil both in production

and during use in high voltage equipment. Sulfur compounds are part of any fossil oil type, in varying quantity. The amount may vary from tenths of a percent to as much as 20% by weight [1].

Fractional distillation causes much of the sulfur compounds to concentrate in the oil fractions and residual products.



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The following are the main classes of sulfur compounds in oil:

- mercaptans (RSH), where R is a radical of the corresponding paraffinic hydrocarbon with straight or branching chain, or a cyclic hydrocarbon radical (aromatic or naphthenic);
- sulfides (R-S-R1), where R and R1 are radicals of the corresponding hydrocarbons;
- disulfides (R-S-S-R1);
- thiophenes, compounds based on pentatomic ring with a sulfur atom.

Sulfur can be present in seals (rubber gaskets) used in transformers [2].

Manufacturers of sealing materials have recently been undertaking much effort to remove sulfur at the stage of material solidifying, but occasionally the amount of sulfur in gaskets is still high.

Sulfur can also be contained in glue used in the making of transformer cores and in copper [3]. Only one case of sulfur compounds from such glue

causing serious corrosion problems in a transformer has been registered so far. The content of sulfur in copper is usually low and does not cause any serious problems.

Another possible way for the sulfur to get into the transformer is the human factor. This includes using hoses which have been used before to pump another oil product with increased sulfur content, or hoses made from high sulfur content materials.

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## Some sulfur compounds are known to have a positive effect on transformer oil performance, such as methyl phenyl sulfide and $\alpha$ -naphthyl thiophane, which improve the oxidation stability of the insulation fluid.

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### Corrosive sulfur: The history

The problem of corrosive sulfur and its compounds in transformer oil was first spoken of in the 1940s [4]. However, the problem has been largely ignored until the early 1990s [5].

In the early 2000s, transformer failures were reported in certain geographical areas [6]. These failures had something in common, and the disassembly of the failed windings into separate turns revealed glossy sediment on portions of wire insulation; the sediment consisted of copper sulfide, Cu<sub>2</sub>S. Since electric conductivity of copper sulfide is much higher than that of oil and paper, this substance reduces the dielectric strength of the insulation, which in turn causes transformer failure. Corrosive sulfur has a negative impact not only on metal conductors and surfaces, but also on insulation paper. In 2005 CIGRE created a special group, A2.32, which researches the problem of Cu<sub>2</sub>S. The group's work resulted in the publication of technical brochure No. 378, *Copper Sulphide In Transformer Insulation*, in 2009.

The brochure describes a two-stage reaction which forms copper sulfide in the transformer as the most reliable and complete theory. At the first stage, oil soluble copper compounds, dibenzyl disulfide (DBDS) are found. Then these compounds diffuse through the insulation oil and can be accumulated on the paper.

At the second stage, these compounds break producing copper sulfide (I). The importance of dibenzyl disulfide in transformer corrosion is noted in many research works [7].

The topic was further researched by the CIGRE A2.40 working group. In 2015, the results were published in brochure No. 625, *Copper Sulphide Long-term Mitigation and Risk Assessment*. It also includes information on yet another malfunction caused by corrosive sulfur. Corrosive sulfur can react with the silver surfaces of switch contacts, forming silver sulfide, Ag<sub>2</sub>S. Ag<sub>2</sub>S is accumulated on the contacts and enters transformer oil during OLTC operation. It can cause serious OLTC damage and lead to transformer winding failures [8].

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## Sulfur can be present in seals (rubber gaskets) used in transformers, in glue used in the making of transformer cores, and in copper. Another possible way for the sulfur to get into the transformer is the human factor.

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The CIGRE document No. 625 also states that 10 mg/kg of DBDS in transformer oil is sufficient to contaminate transformer insulation paper.

### Protecting the transformer from corrosion

Literature mentions several main methods of protecting the transformer against corrosive sulfur and its compounds. Some of them are passivation, oil change and adsorption purification.

Passivation involves the use of chemicals which form a protective layer (film) on copper surfaces, preventing the reaction of copper ions with sulfur. The problem with this method is that there are different copper alloys in transformers, and each passivator acts differently with each alloy. Another important factor is that copper is not the only metal susceptible to sulfur in the transformer. Iron, aluminum, zinc, nickel and magnesium all react with sulfur forming their respective salts, which also degrade transformer performance. Passivator in general is a preventive measure, which can impede copper corrosion, but cannot restore corroded copper and paper contaminated with Cu<sub>2</sub>S.

Another method for eliminating the influence of sulfur and its compounds on the transformer is oil change. However, even with a full oil change, as much as 10% of old oil usually remains in the transformer, and if the oil contains sulfurous contaminants, they will contaminate the fresh oil. This makes additional transformer washing necessary, which still has no effect on the consequences of corrosion.

Efficient removal of sulfur and sulfur compounds with the help of various adsorbents, such as Fuller's earth, activated charcoal and synthetic adsorbents, became the subject of research in the early 2000s. The results indicated that the adsorption method is not a complete solution to the problem of corrosive sulfur and its compounds in transformers. However, if the process includes several stages, where a special chemical is used in one stage and Fuller's earth in the other,

it is possible to completely remove this contaminant [9].

The ability of some metals to absorb dibenzyl disulphide has also been researched with the objective of making special filters to reduce the concentration of sulfur in transformer oil. One article [10] states that zircon can reduce the concentration of DBDS in transformer oil from 48 ppm to 9 ppm. The objective of this work is to find a simple, efficient and environmentally friendly process of dibenzyl disulfide removal from insulation oil. We believe it can be achieved with sorbents alone, without other chemicals.

**Researching the abilities of sorbents to remove DBDS from insulation oils**

Several samples of transformer oil with sulfur and DBDS content of 11.6 ppm and 88 ppm, respectively, were prepared for the test. The samples were processed in a special laboratory vacuum machine, which consists of a regeneration pod, a vacuum chamber, a vacuum pump, and a vacuum meter to control the pressure in the vacuum chamber. The regeneration pod is equipped with an electric heater and a temperature sensor.

The regeneration pod is filled with adsorbent. The vacuum pump creates vacuum in the vacuum chamber. The regeneration pod is filled with oil, then the heater is engaged to increase oil temperature to 65°C. Then, vacuum pulls the oil through the adsorbent and into the vacuum chamber. Regenerated oil is drained from the chamber through a valve.



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**It seems viable to use a mix of multiple adsorbents for sulfur removal, each component being especially efficient for specific type of sulfurous substances. This means a synthesis of sulfur removal and regeneration technologies, as adsorbents remove not only sulfurous compounds, but also the contaminants resulting from oil aging.**

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The sorbents used were Fuller’s earth and a special mineral clay. Elemental sulfur and DBDS content were measured in compliance with IEC 62597-1 ed.1 (2012-08) and IEC TR 62697-3 (2018). The results are listed in Table 1.

The information in the table shows that using the special clay mineral to process oil (150 ml to 150 g ratio of oil to adsorbent) removed DBDS completely. The amount of elemental sulfur in the oil remained unchanged.



**Table 1.**  
*Elemental sulfur and DBDS content in transformer oil samples before and after processing*

Sample	Purification process	DBDS, ppm	Elemental sulfur (S <sub>8</sub> ), ppm
1	Original untreated oil	88.0	11.6
2	1.2 liters of oil per 100 g of Fuller’s earth (four passes)	17.8	11.6
3	200 ml of oil per 50 g of special clay sorbent	3.9	No measurement was made
4	200 ml of oil per 150 g of the special mineral clay	Not detected	11.6

## Conclusions

The research shows that using the special natural adsorbent makes it possible to completely remove dibenzyl disulfide from the oil in one pass from at least 88 ppm concentration, which is almost nine times of the maximum limit.

Fuller’s earth made possible the reduction of DBDS content to 17.8 ppm (after four passes), but not its complete removal. It seems viable to use a mix of multiple adsorbents for sulfur removal,

each component. Our experience in development and construction of oil regeneration equipment allows us to design desulfurization equipment which can run on energized transformers, eliminating the long downtime often required for oil processing. Besides, the suggested technology is more environmentally friendly, as it does not involve chemicals, while the performance of saturated adsorbent can be restored in the process of reactivation directly in the regeneration machine.



**There are several methods of protecting the transformer against corrosive sulfur and its compounds, including passivation, oil change and adsorption purification.**



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