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Stability and reactivity of sulfur compounds against copper in insulating mineral oil: definition of a corrosiveness ranking

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ABSTRACT

Corrosive sulfur is a well-known critical issue for mineral insulating oils used in power transformers. The objective of this work is to study the reactivity of different groups of sulfur containing compounds (aliphatic and aromatic mercaptans, sulfides, disulfides, thiophenes) that may be present in insulating oils. The stability of nine compounds, pertaining to the aforementioned groups, was investigated with regards to temperature and aging time, under oxidative and inert atmosphere, in order to simulate the natural aging of both hermetically sealed or free breathing type transformers. Their reactivity against copper was also investigated. A gas chromatography atomic emission detection method was optimized to quantify the consumption of each compound. The tendency of 22 sulfur compounds to react with copper and form copper sulfide was quantitatively assessed at different temperatures. The resulting corrosiveness ranking for sulfur compounds families differs from what is usually reported in literature, and was proven to be temperature dependent.

KEYWORDS: insulating oil, corrosive compounds, corrosive sulfur, corrosiveness ranking

INTRODUCTION

An increasing occurrence of copper sulfide formation in paper-insulated windings of power transformers and shunt reactors has been observed in the last decades. Some failures that occurred in large power transformers have been ascribed to this phenomenon, as a result of chemical reactions occurring between copper conductors and insulating materials (Kraft paper and oil).¹⁻³ It is worldwide accepted that corrosion is mainly promoted, at the standard operating temperature of the transformer, by the reaction of some forms of sulfur, defined as "corrosive sulfur", and the naked copper surfaces, resulting in the formation of copper sulfide.⁴

Sources of sulfur compounds are numerous. Crude oil, from which insulating oils are obtained, has a relatively high sulfur content, a great deal of which is reactive towards copper components of the transformer.⁵ Thanks to the improvements in the petroleum refining processes (hydro-treating) and the increasing demand of petroleum derivatives with a low sulfur content, in the last 25 years there was a marked reduction of the concentration of total sulfur in insulating oils.⁶⁻⁸ Nowadays, the amount of sulfur contained in a typical transformer oil may range from 0.001 to 0.5 %.⁹ As a side effect, the same refining processes, that reduce the total amount of sulfur, lead to a decrease in the concentration of aromatic and hetero-atom compounds that act as natural antioxidants.^{10,11} This sometimes requires the restoring of part of the original sulfur compounds by the so-called "back-blending", a common practice that entails the mixing of heavier refining streams (rich in sulfur and aromatic compounds) with the highly refined base oil. Among the crude oil -derived sulfur compounds some are beneficial to the oils, as they act as retardants or passivators in oxidation reactions, but others may cause corrosion.⁴ As a consequence, the reduction in total sulfur amount apparently promotes an increase in the occurrence of corrosive sulfur.

Another source of corrosive sulfur in insulating oil can be the chemicals usually added to improve the antioxidant properties.¹²

As a result of the above described causes, sulfur can be present either in the elemental form or contained in organic molecules (e.g.: thiophenes, disulfides and polysulfides, thio-ethers and mercaptans). Not all these substances are corrosive, or have the same reaction rate against copper: the degree of corrosiveness of a mineral oil is usually a function of the type and concentration of compounds present, the working temperature and the presence of oxygen.⁴

A generally accepted corrosiveness ranking is: $S_x > R-SH > R-S-R \gg R-S-S-R \gg$ thiophenes.¹³ Elemental sulfur (usually in the S_4 or S_8 form) is considered highly reactive against copper, while disulfides are relatively stable and thiophenes are not reactive. Nevertheless, very few data about their reactivity and degradation trend are available in literature. Jian et al.¹⁴ investigated the effect of corrosive sulfur at different temperatures, and Lukic et al.¹⁵ studied different ways to remove sulfur compounds from insulating oils. Unfortunately neither of them detailed the types of sulfur species present. Maina et al.¹⁶ started in 2009 to study the degree of corrosiveness of dibenzyl disulfide. Recently, only Kamishima¹⁷ investigated how changes in the molecular structure of sulfur compounds in mineral insulating oils affect their corrosiveness.

The fact that the majority of the studies on corrosiveness in mineral insulating oils were focused on dibenzyl disulfide (DBDS)^{5, 18-20}, a sulfur compound considered relatively stable¹³, reveals that the traditional reactivity scale may not reflect the reality. Previous studies highlighted that DBDS reduction to benzyl mercaptan can result in more corrosive properties^{16,10} and that by-products such as bis-benzyl and dibenzyl sulfide can be present in in-service mineral oils.^{16,21} Finally, although the corrosiveness of almost 90 % of corrosive oils in transformers is determined by DBDS,¹⁶ a significant amount of insulating oils were found to be corrosive, and

namely capable to transfer copper sulfide onto the Kraft paper tapes, independently of the presence of DBDS. This shows that most of the sulfur compounds responsible for the corrosion process remain unidentified.

For the above mentioned reasons, the aim of this work was to investigate the stability and the potential corrosive behavior of different types of organic sulfur compounds towards copper and paper insulation. Therefore, different reaction conditions were explored: the behavior of the tested sulfur compounds was investigated at temperatures ranging from 80 to 200 °C, in the presence and absence of oxygen and bare copper. Experiments were conducted at different contact times (72 – 240 hours) to elucidate the rate of depletion of each compound. A corrosiveness ranking was assessed by determining the total corrosive sulfur (TCS) for each compound at different temperatures. The corrosiveness of each compound, obtained by TCS test, was compared with the results of the official method for corrosive sulfur detection (ASTM D1275 B).

EXPERIMENTAL SECTION

Materials

Isooctane was from Panreac (Barcelona, Spain), Dibenzothiophene ($\geq 99\%$, DBTf), Dodecyl methyl sulfoxide (98 %, DcMSOx), Phenyl vinyl sulfide (97 %, PVS), sec-Butyl sulfide (98 %, sBS), Dibenzyl disulfide (98 %, DBDS), Diphenyl disulfide (99 %, DPDS), Isopropyl disulfide (96 %, IPDS), Benzyl mercaptan (99 %, BMt), Benzene-1,3-dithiol (99 %, BDT), Butylmercaptan (99 %, BuMt) and Heptylmercaptan (98 %, HeMt) were from Sigma-Aldrich (St. Louis, MO, USA). Dibenzyl sulfoxide (DBSOx), Dibutyl sulfoxide (DBuSOx), Dibenzyl sulfide (DBS), 2-Methyl-1,3-dithiane (MeDT), Dodecyl Mercaptan (DCMt), Hexadecyl

Mercaptan ($\geq 95.0\%$, HDMt), 1,2-Ethanedithiol (EtDt) and Cyclohexanethiol (97 %, CET) were from Acros Organics (Thermo Fisher Scientific, Geel, Belgium). Finally, Pentamethylene Sulfide (PMeS) and Butyl Disulfide (BuDS) were from Wako Pure Chemical Industries (Osaka, Japan), and Thioanisole (TAS) was from VWR International (Milano, Italy).

Chemical structures and abbreviations of each compound are collected in Table S1 of the Supporting Information.

The samples were prepared in a sulfur-free light mineral oil (Sigma Aldrich, Milan, Italy— $d(25\text{ }^\circ\text{C}) = 838$ to 854 kg/m^3 ; kinematic viscosity at $40\text{ }^\circ\text{C} = 14.2$ to 17.0 cSt) at a concentration of 40 mg/kg expressed as elemental sulfur for each compound. Samples were diluted 1:10 v:v in isooctane before injection.

For the reactivity study and for the ASTM test, copper foils of $4\text{ mm} \times 10\text{ mm}$ and $6\text{ mm} \times 25\text{ mm}$, respectively were used.

Vials of 20 mL (22 mm diameter) with PTFE/butyl rubber septa and aluminum crimp caps (Agilent) were used for total corrosive sulfur (TCS) determination.

Methods

The amount of each compound during the corrosiveness study was determined using a 6890 Model gas chromatograph (Agilent Technologies, CA, United States) equipped with a MPS2 autosampler (Gerstel GmbH, Germany) and coupled with an Atomic Emission Detector (AED) from Joint Analytical Systems GmbH, Germany. A HP-1 Methyl Siloxane capillary column ($60\text{m} \times 250\text{ }\mu\text{m} \times 0.25\text{ }\mu\text{m}$) from Agilent was used.

Corrosiveness studies

Reactivity study in white oil (light mineral oil). With the objective of simulating the stress conditions to which sulfur compounds may be subject in power transformers during service, the influence of different parameters was investigated: temperature (to simulate the thermal stress), presence of oxygen (to understand the influence of the conservator segregation mode—sealed or free breathing) and contact with copper conductor.

The Design Of Experiments (DOX) can be detailed as follows: 1.5 ml of white oil containing nine selected compounds (dibenzothiophene, dibenzyl sulfide, phenyl vinyl sulfide, dibenzyl disulfide, diphenyl disulfide, butyl disulfide, benzyl mercaptan, dodecyl mercaptan, hexadecyl mercaptan) at 40 mg/kg each (expressed as elemental sulfur) were put in 2 ml glass vials for gas chromatography, sealed with rubber septum and artificially aged at 80°C, 100°C, 120°C, 150°C, 200°C. At each temperature, aging times of 36, 72, 144 and 288 hours were applied.

The behavior of the nine compounds was studied, according to the procedure detailed above, under the following conditions:

-thermal aging (Heating): 1.5 ml of the solutions aged in sealed vials, without contact with air or copper;

-thermal-oxidative aging (Heating + O₂): 1.5 ml of the solutions aged in sealed vials, intake of air through a stainless steel needle (i.d. 0.8 mm) breaking through the septum without contact with copper;

-non-oxidative corrosion (Heating + Cu): 1.5 ml of the solutions aged in sealed vials, containing a piece of naked copper strip (72 mm² total surface) , without contact with air;

-oxidative corrosion (Heating + O₂ + Cu): 1.5 ml of the solutions aged in sealed vials, intake of air through a stainless steel needle breaking through the septum (i.d. 0.8 mm), and containing a piece of naked copper strip (72 mm² total surface).

Copper strips were polished before use with sand-paper and acetone; the procedure was derived by method ASTM D1275.

The residual amount of each compound was determined by an optimized GC-AED method (optimized experimental conditions are reported in Table S2 of the Supporting Information) on diluted samples (1:10 with isooctane) comparing chromatographic peak areas before and after aging.

Corrosiveness ranking by total corrosive sulfur (TCS) determination. To estimate the tendency of different families of sulfur compounds to form copper sulfide as a consequence of the contact with bare copper surfaces, we measured the amount of Cu₂S formed by 22 different compounds (listed in Table S1, Supporting Information) under different temperature conditions. This test was applied as a modification of the Total Corrosive Sulfur (TCS) Test previously described²². Individual solutions, containing each sulfur compound at 40 mg/Kg (expressed as elemental sulfur), were prepared in light mineral oil; aliquots of 10 g of oil were put in contact with 3 g of copper powder and heated and stirred for 12 hours, under Argon atmosphere. Finally, the oil was pipetted out and the powder rinsed twice with isooctane and pentane. Copper sulfide was formed and then oxidized to sulfate by KNO₃ at 370°C for 2 hours. Sulfate ions were extracted in deionized water and measured by turbidimetry.

The resulting TCS is calculated according to the following equation:

$$\text{TCS} = [(\text{C}_{\text{Sulfate}} / 96.06) \times \text{V}_{\text{sol}} \times 32.07] / \text{kg}_{\text{oil}}$$

where C_{Sulfate} is the sulfate concentration (mg/L), V_{sol} the volume of the solution in which sulfates are extracted (L) and kg_{oil} is the weight of oil sample. The corrosiveness has been calculated as corrosion yield, using the formula:

$$R_c = 100 \times [\text{TCS}]/[\text{TCS}]_{\text{theoretical}}$$

where $[\text{TCS}]_{\text{theoretical}}$ is the total corrosive sulfur value for a quantitative conversion of the sulfur compound in Cu_2S .

TCS has been applied as an internal method, and its reproducibility has not yet been evaluated at the time of preparation of this paper. All the results reported in this paper were obtained as average of duplicate tests (spread between the two replicates ranged from 3 to 25 %). TCS' reproducibility should be expected to be quite large, due to the number of steps involved inside the test procedure. Therefore, results obtained by TCS test shall be considered as comparisons of the order of magnitude of the corrosiveness yield of each individually tested compound.

TCS tests were performed at the following temperatures: 80 °C, 100 °C, 120 °C, 150 °C and 180°C.

Corrosiveness estimated by standardized method. Each solution of the 22 compounds studied, containing 40 mg of elemental sulfur per kg of light mineral oil was tested by an official method (ASTM D1275 B²³) to evaluate the corrosiveness. Accordingly with ASTM D1275 B procedure, a naked copper strip is put in contact with 250 ml of oil at 150 °C for 48 hours. The oil is classified corrosive when the copper sulfide film formed upon the conductor surface is black, dark grey or dark violet colors, according to the color scale given in the ASTM D130/IP 154.

In order to verify the absence of corrosive effect from the technical oil, a blank sample (technical new oil without sulfur compounds) was processed.

In order to compare the results obtained in the reactivity study (see Results and Discussion section) and in the corrosiveness ranking study (see Results and Discussion section), ASTM D1275 B method was performed at different temperatures: 80°C, 100°C, 120°C, 150°C and 180°C.

RESULTS AND DISCUSSION

Selection of sulfur compounds

The behavior of 22 substances belonging to the following families of sulfur compounds were investigated (table S1): thiophenes (1), sulfoxides (3), sulfides (6), disulfides (4) and mercaptans (8). Compounds were chosen in order to cover the corrosiveness scale and to include molecules actually found in in-service transformer oils (DBDS, DBS, BMt and DBTf).

In order to correlate the structure with the corrosiveness, within each class, where possible, both aliphatic and aromatic compounds were selected.

Reactivity study

Among possible faulty conditions that can occur in transformers, overheating is one of the most important.²⁴ Copper sulfide formation on conductors and Kraft paper tapes has been often related to increased temperatures, determined by either faulty conditions or severe thermal profile.²⁵ Consequently, it is important to assess the stability of different sulfur compounds under different thermal stress conditions.

The reactivity study was performed on nine selected compounds (BMt, PVS, BuDS, DCMt, DBTf, DBS, DPDS, HDMt, and DBDS) representative of the above mentioned classes. A GC-AED method was optimized with the aim of quantitatively estimating the consumption of each

compound after the aging step. Analytical conditions are summarized in Table S2 (Supporting Information). This method allowed the separation and detection of the nine compounds, in 46 minutes (Figure 1).

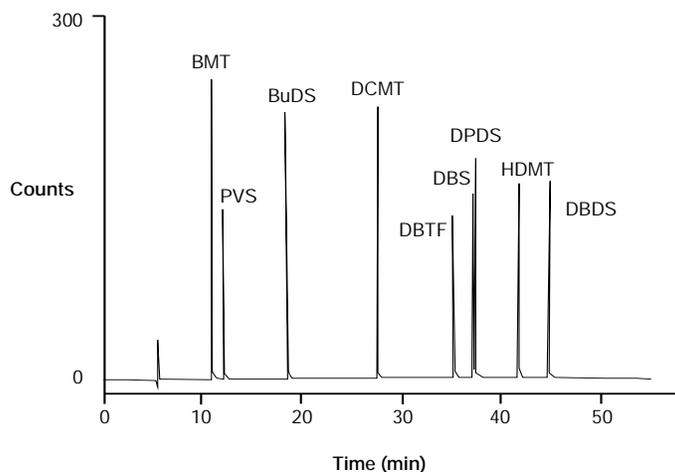


Figure 1: Gas chromatographic separation of the nine selected sulfur compounds. Chromatographic conditions are reported in Table S2 (Supporting Information).

The reactivity of BMT, PVS, BuDS, DCMt, DBTf, DBS, DPDS, HDMt, and DBDS was studied at five different temperature levels: 80°C, 100°C, 120°C, 150°C and 200°C. These levels were chosen to include the operating temperature of a transformer under normal conditions (< 105°C), and simulate a slight overheating (105°C-200°C), typical of many electrical in-service equipment. The role of oxygen and copper in degradation was also studied.

As a general consideration, compounds degrade faster with the increase of reaction conditions harshness (augmented temperature and time of exposure). It has been generally observed that harder reaction conditions promote a faster compound degradation, especially if oxygen and copper are present. This behavior is shown for DBDS (figure 2), as a general example.

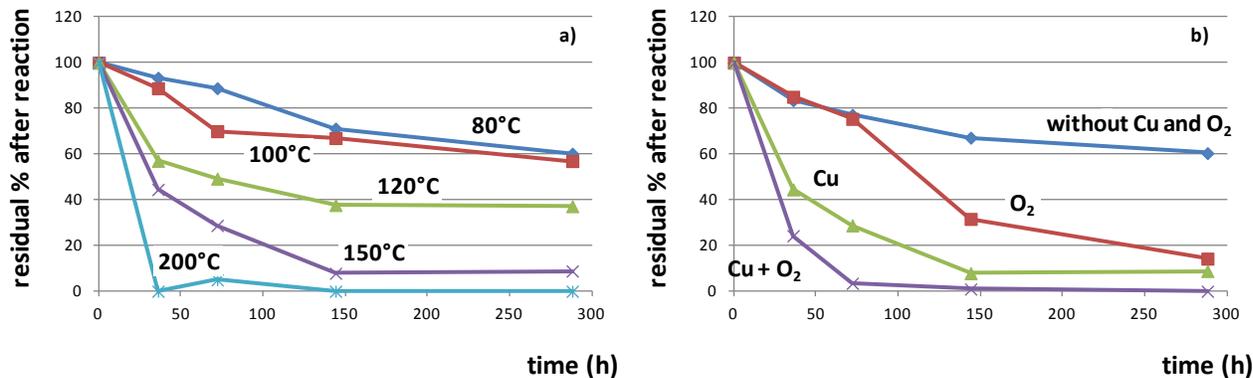


Figure 2: Degradation of DBDS. Conditions: (a): thermal aging in presence of copper; (b): oxidative degradation in presence and without copper at T= 150 °C.

The behavior of the various classes of substances, at different temperatures, is hereafter described (Figure 3a-3e).

Reactivity and depletion rate at 80 °C (figure 3a): mercaptans (BMt, DCMt, HDMt) are stable with temperature and moderately influenced by the presence of oxygen. Butyl mercaptan and phenyl vinyl sulfide are the most and the least stable compounds, respectively. Mercaptans and, to a minor extent, disulfides exhibit reactivity towards copper; in presence of copper, reactivity of disulfides is fairly influenced by oxygen. Conversely, dibenzylsulfide and mercaptans degradation is enhanced by oxygen in the presence of copper.

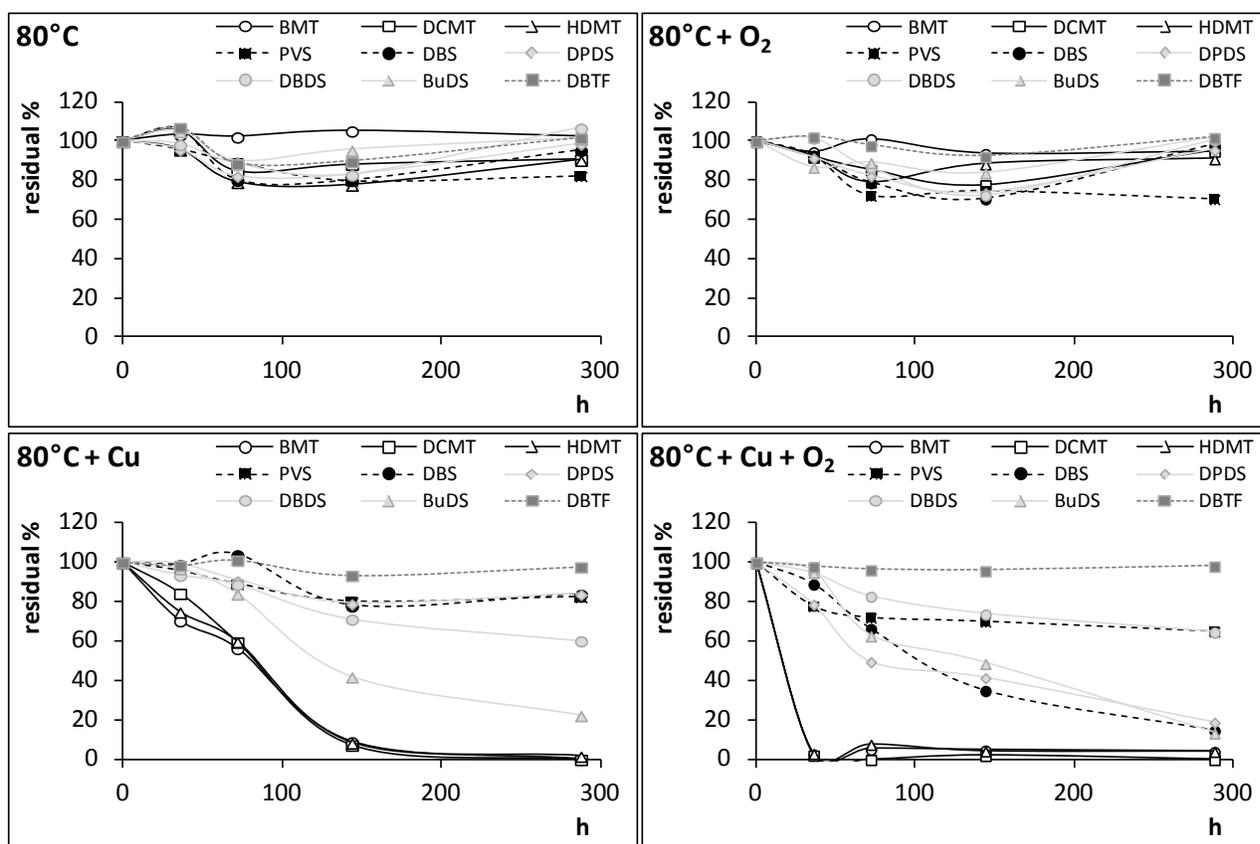


Figure 3a. Thermal and oxidative degradation in presence and without copper at 80 °C

Reactivity and depletion rate 100 °C (figure 3b): mercaptans and disulfides reacts with metal at exposure times lower than what observed at 80°C. The reactivity of sulfides towards copper is observed only in presence of oxygen. As a general consideration, aromatic compounds seem to be more stable than aliphatic ones (e.g: compare the behavior of dibenzyl disulfide with butyl disulfide).

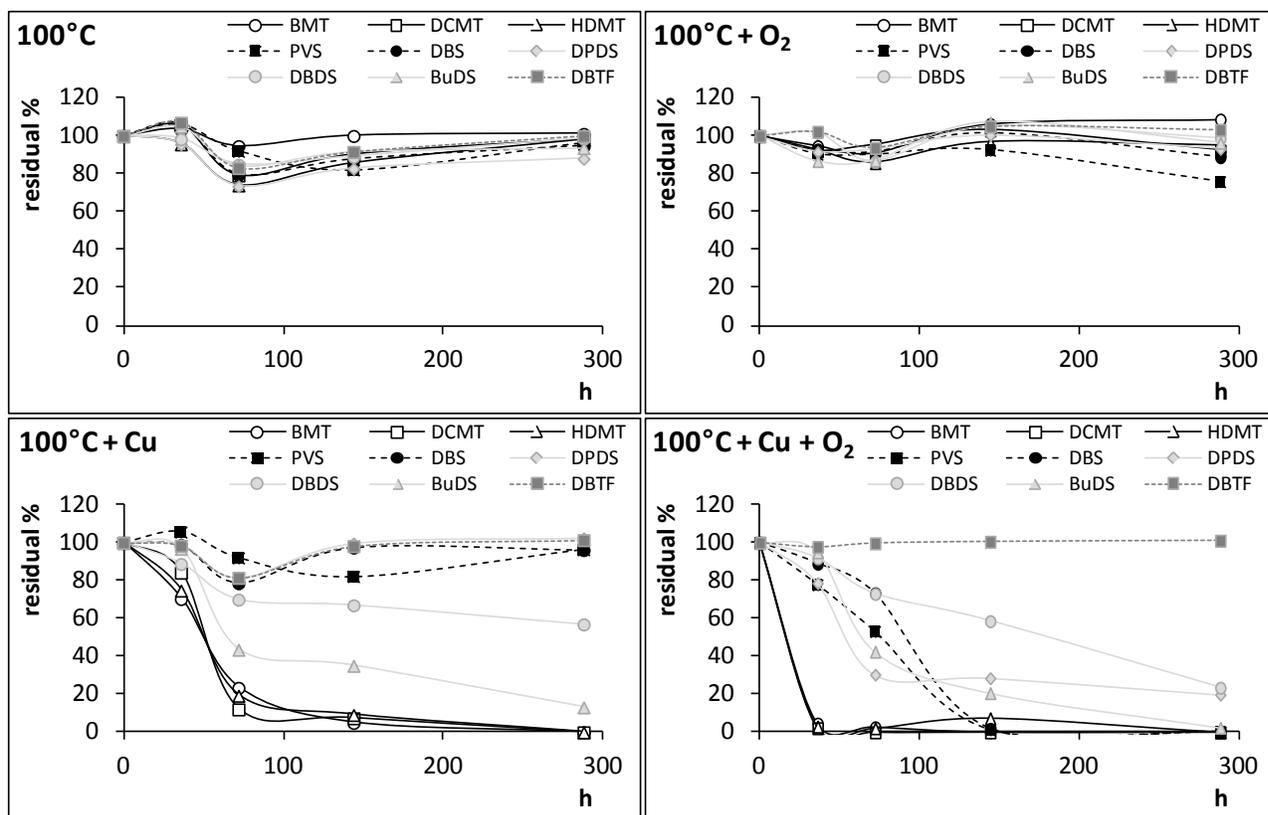


Figure 3b. Thermal and oxidative degradation in presence and without copper at 100 °C

Reactivity and depletion rate 120 °C (figure 3c): heating under inert atmosphere does not induce appreciable depletion of the sulfur compounds. If oxygen is present, some sulfides and mercaptans are significantly consumed. All the mercaptans and disulfides have a strong reactivity towards copper.

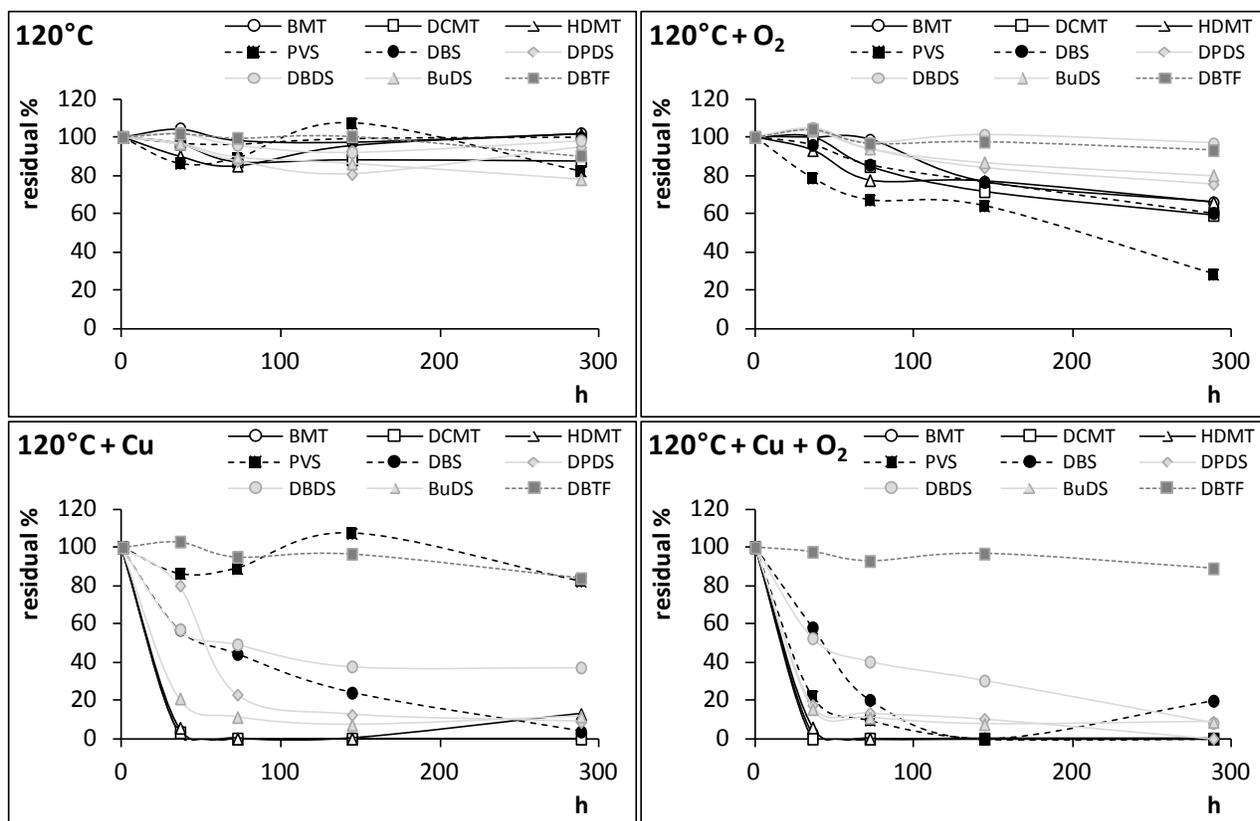


Figure 3c. Thermal and oxidative degradation in presence and without copper at 120 °C

Reactivity and depletion rate 150 °C (figure 3d): at this temperature, thermal degradation occurs. Oxidative degradation as well as reactivity towards copper is enhanced; in particular, mercaptans are totally degraded within 36 hours of reaction, showing a higher corrosiveness effect compared with sulfides and disulfides. It is worth mentioning that dibenzothiophene is the only compound that does not show reactivity towards copper.

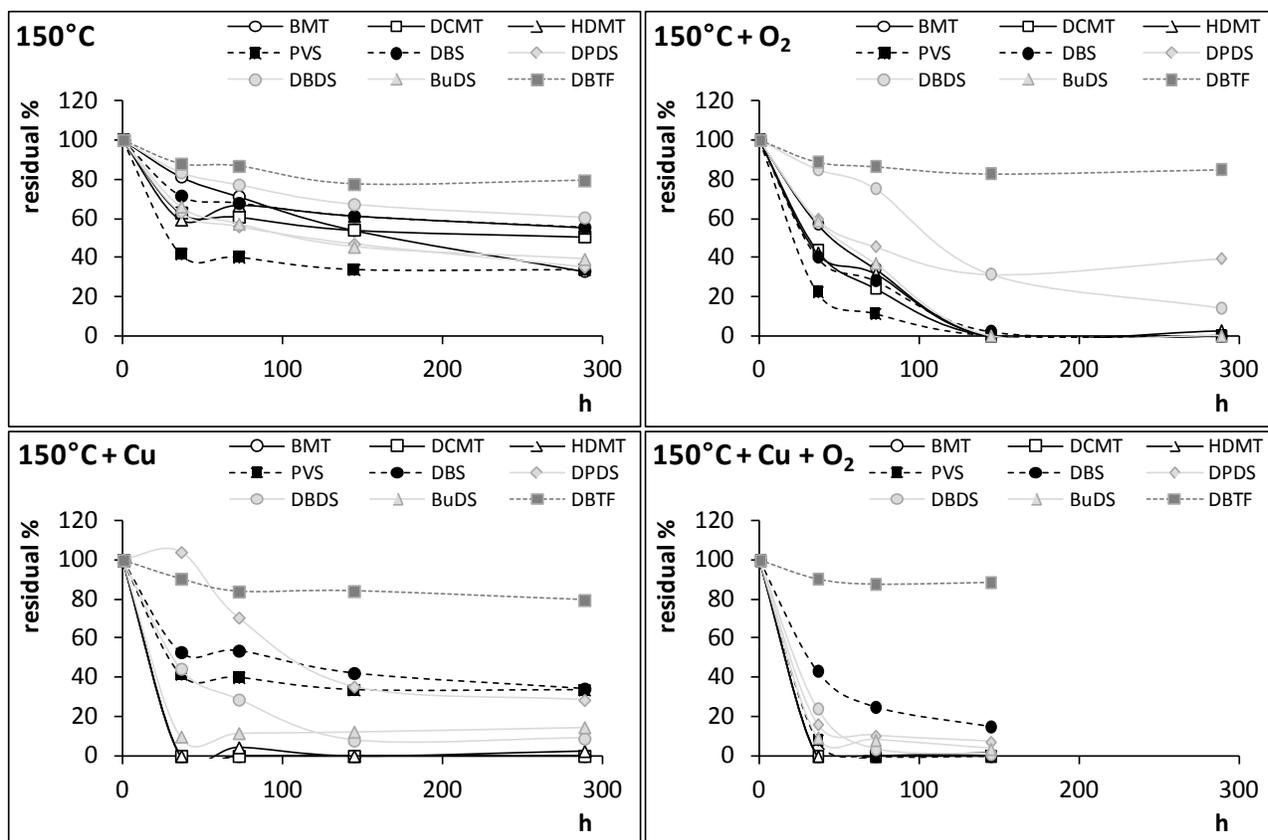


Figure 3d. Thermal and oxidative degradation in presence and without copper at 150 °C

Reactivity and depletion rate 200 °C (figure 3e): strong thermal degradation is observed for all compounds, except for dibenzothiophene. In the presence of oxygen 80 % of DBTF is still unreacted (50% residual after 288 hours also in oxidative conditions). These data suggest a non-corrosive behavior of dibenzothiophene, even in the event of harsh temperature conditions of open-air transformers. This was also recently suggested by Kamishima et al.,¹⁷ who have evaluated the absence of corrosiveness of a dibenzothiophene fortified oil through ASTM D1275 B, and verified the corresponding negligible formation of sulfur on the surface of a copper strip by wavelength dispersive X-ray fluorescence.

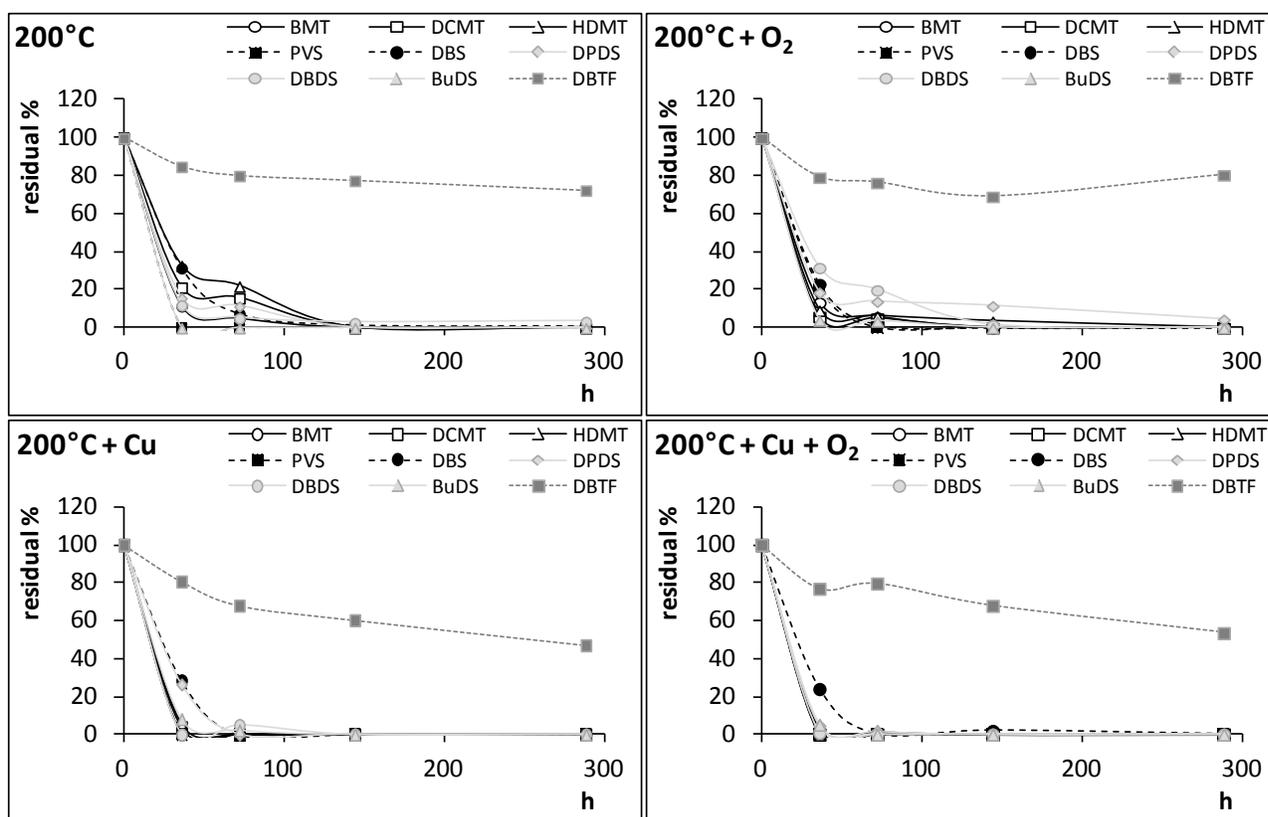


Figure 3e. Thermal and oxidative degradation in presence and without copper at 200 °C

To summarize, it can be stated that all nine sulfur compounds are quite resistant to thermal and oxidative degradation, at the temperatures close to the normal working condition of transformers (80°-120°C). As a general rule, air (oxygen) accelerates the decomposition at high temperatures. For a temperature higher than 120°C, other than DBTF, only the compounds belonging to the disulfide family remain stable (especially the aromatic ones), while substances in the mercaptans and sulfides families are quickly depleted, in particular in the presence of oxygen.

Mercaptans exhibit a high reactivity to copper even at low temperature, whereas sulfides and disulfides require a higher temperature (above 120°C). This result is in accordance with the theory of a peculiar reaction path of DBDS, postulated by some researchers¹³, that ascribes its corrosiveness towards copper to DBDS degradation to benzyl mercaptan (BMT).

The copper pieces collected after the aging experiments gave a qualitative evaluation of the corrosion phenomena (figure 4).

		Ageing time (hours)							
		36h		72h		144h		288h	
Temperature (°C)	80								
		Cu	Cu+O2	Cu	Cu+O2	Cu	Cu+O2	Cu	Cu+O2
	100								
		Cu	Cu+O2	Cu	Cu+O2	Cu	Cu+O2	Cu	Cu+O2
	120								
		Cu	Cu+O2	Cu	Cu+O2	Cu	Cu+O2	Cu	Cu+O2
	150								ND
		Cu	Cu+O2	Cu	Cu+O2	Cu	Cu+O2	Cu	Cu+O2
	200								
		Cu	Cu+O2	Cu	Cu+O2	Cu	Cu+O2	Cu	Cu+O2

Figure 4. Images of copper conductors after the aging experiments according to the DOX.

Copper pieces become progressively darker with increasing temperature and aging time, mainly due to the formation of Cu_xO , Cu_xS_y and other insoluble compounds. It is noteworthy that, at 80°C and 100°C, the presence of oxygen considerably enhances copper corrosion, in

particular after 144 and 288 hours. At higher temperature no particular differences are observed between the pieces in contact with air and those aged without direct exposure to air.

Finally, it can be hypothesized that oxidation and corrosiveness are two competitive reactions: compounds with a lower thermal stability and/or more prone to oxidation should be less corrosive at high temperatures, where the thermal/oxidative degradation competes with the corrosive reaction towards copper.

According to the same hypothesis, compounds with higher thermal stability, but having a good affinity to copper, should show enhanced corrosiveness at higher temperatures.

Corrosiveness ranking

The reactivity study described in the previous paragraph provides a rough corrosiveness ranking for the families of tested compounds. In particular, for temperatures comprised between 80 and 120 °C, mercaptans appear to be the most corrosive compounds, whereas between 150 and 180 °C, the highest corrosiveness properties are exhibited by disulfides. To deeply investigate the dependence of corrosiveness on temperature, and correlate it with the reactivity data previously obtained, the TCS method was performed at the same temperatures used for the reactivity study. In this way, the corrosiveness of each compound towards copper was calculated (and expressed as yield of copper sulfide formed against the stoichiometric theoretical amount of available sulfur), thus allowing to define a corrosiveness ranking of the investigated compounds at the considered temperatures.

As reported in table 1, the results are in agreement with what observed during the reactivity study. In detail, at 80 °C (temperature typical of transformers operating at normal conditions),

only mercaptans show corrosion towards copper, with a yield proportional to the number of sulfur atoms.

Table 1. Corrosion yield for all the 22 sulfur compounds calculated according to TCS tests.

Class	Compound	Corrosion yield (%)				
		80°C	100°C	120°C	150°C	180°C
Thiophenes	Dibenzothiophene	N.D.	N.D.	N.D.	N.D.	N.D.
Mercaptans	1,2-Ethanedithiol	64.2	49	51.5	35.7	51.9
	Benzene-1,3-dithiol	60.6	29.8	78.4	77.5	79.5
	Dodecyl mercaptan	33.6	66.2	32.9	50	75.4
	Butyl Mercaptan	30.4	28	24.5	45.7	58.9
	Cyclohexanethiol	26.5	30.8	41.8	80.5	91.8
	Benzyl mercaptan	24.8	0	50.8	67.5	60.3
	Hexadecyl mercaptan	23.9	7.3	23	35	76.8
	Heptyl mercaptan	8	0	34.8	73.8	63.5
Sulfoxides	Dibenzyl sulfoxide	N.D.	N.D.	N.D.	55	100.2
	Dibutyl sulfoxide	N.D.	N.D.	N.D.	45.4	81.9
	Dodecyl methyl sulfoxide	N.D.	N.D.	N.D.	45.2	69
Sulfides	2-Methyl-1,3-Dithiane	N.D.	N.D.	11.3	19.2	66.7
	Phenyl vinyl sulfide	N.D.	22.6	34.7	15	55.3
	Dibenzyl sulfide	N.D.	N.D.	N.D.	N.D.	77.8
	sec-Butyl sulfide	N.D.	N.D.	N.D.	N.D.	N.D.
	Pentamethylene sulfide	N.D.	N.D.	N.D.	N.D.	N.D.
	Thioanisole	N.D.	N.D.	N.D.	N.D.	N.D.
Disulfides	Dibenzyl disulfide	N.D.	47.4	73.8	90	99.7
	Isopropyl disulfide	N.D.	N.D.	23.7	71.8	95.6
	Butyl disulfide	N.D.	N.D.	16.4	65	75.2
	Diphenyl disulfide	N.D.	23.8	27.4	45	54.6

N.D. = Not Detectable. Detection Limit for TCS was fixed at 2 mg/kg of elemental sulfur, thus corresponding to 5 % under the experimental condition applied.

At 100 °C, sulfides (PVS) and disulfides (DBDS and DPDS) begin to exhibit reactivity against copper, even if mercaptans remain on average the most corrosive compounds. Only at moderately high temperature (120 °C) all disulfides are corrosive, and their corrosiveness yield, in particular in the case of an aromatic molecule like DBDS, becomes comparable to mercaptans.

At 150 °C an inversion in the corrosion scale is observed since disulfides become more reactive than mercaptans; the same behavior can be observed for sulfoxides that show, in particular the aromatic ones, to be aggressive towards copper.

Finally, at 180 °C (a temperature that simulates overheating conditions, as thermal fault type T1 as defined in IEC 60599) the corrosion effect further increases for all the families of compounds, and the conversion of some disulfides (DBDS, isopropyl disulfide) and sulfoxides (dibenzyl sulfoxide) to Cu_2S becomes quantitative (corrosion yield 100%).

According to the results obtained, the following corrosiveness ranking can be proposed (figure 5), where capital letters were used to emphasize a more pronounced corrosiveness:

- 80 °C: MERCAPTANS >>> sulfides \approx disulfides \approx sulfoxides \approx thiophenes;
- 100 °C MERCAPTANS >> DISULFIDES > SULFIDES > sulfoxides \approx thiophenes;
- 120 °C MERCAPTANS \approx DISULFIDES >> SULFIDES > sulfoxides \approx thiophenes;
- 150 °C DISULFIDES > MERCAPTANS > SULFOXIDES > SULFIDES >> thiophenes;
- 180 °C SULFOXIDES \approx DISULFIDES > MERCAPTANS > SULFIDES >> thiophenes.

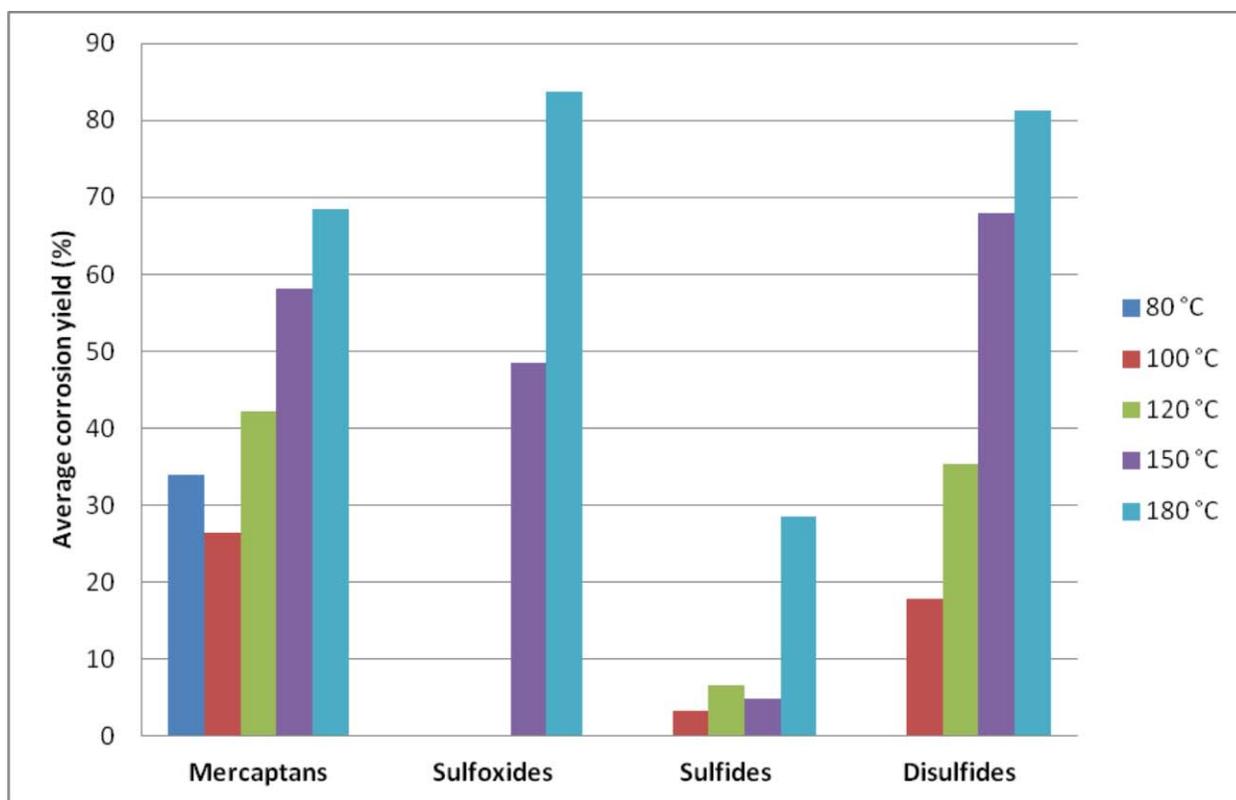


Figure 5. Corrosiveness of family of compounds (averaged on all the investigated compounds) at different temperatures.

The results indicate that up to 120 °C, the -SH group is responsible for the major corrosive effect. Other species (i.e. disulfides or sulfoxides) begin to exhibit relevant corrosiveness only from an aging temperature higher than 150°C. This evidence (deduced from the results obtained under the applied experimental conditions) is in opposition to the classical scale of reactivity based only on the thermodynamic affinity between sulfur compounds and copper.

To investigate the corrosiveness also in the presence of oxygen, some of the studied compounds were selected on the basis of their behavior in the reactivity study and higher values of corrosion provided by the TCS method. For this purpose, the original TCS test was repeated using a septum drilled with a stainless steel needle (i.d. 0.8 mm), allowing air intake.

It can be observed from these data (see Table 2) that corrosiveness increases proportionally with temperature for all the investigated compounds. In agreement with what highlighted by the reactivity study, the presence of oxygen hampers corrosion to a certain extent.

Table 2. Corrosiveness yield for selected sulfur compounds calculated according to TCS tests, performed in presence of oxygen.

Class	Compound	Corrosion yield (%)			
		80°C	100°C	120°C	150°C
Mercaptans	Dodecyl mercaptan	N.D.	32.7	49.6	58.6
	Cyclohexanethiol	7.3	36.3	52.1	74.7
	Benzyl mercaptan	24.9	52.2	67.2	61.9
Sulfoxides	Dibenzyl sulfoxide	N.D.	N.D.	N.D.	23.2
Sulfides	Phenylvinylsulfide	7.3	27.6	22.9	43.9
Disulfides	Dibenzylsulfide	N.D.	N.D.	5.3	5.3
	Dibenzyl disulfide	N.D.	48.7	68.3	75.9
	Diphenyl disulfide	N.D.	42.2	51.2	51.6

N.D. = Not Detectable.

As it can be perceived from data in Table 2, sulfur compounds like aliphatic mercaptans, that showed to be the most easily oxidized (see figures 3a to 3e) even at lower temperatures, have a lower corrosion yield in the presence of oxygen. On the other hand, compounds like DBDS, that are less prone to oxidation, show similar corrosion yield regardless the presence of oxygen. This result confirms the competitive effect of an oxidative atmosphere, and confirms other results obtained by some researchers, that showed how corrosive oils have a peak of reactivity at relatively low oxygen content.²

Comparison with official measurements

Methods available to assess the degree of corrosiveness of an oil upon copper usually imply a visual evaluation after the reaction between the oil and a copper surface. Generally, they can be classified into two families: (i) methods using naked copper strips (e.g. method ASTM D1275), and (ii) methods using paper-wrapped copper conductors (method IEC 62535²⁶). Methods involving paper are aimed at evaluating the capability of the oil to form copper sulfide on the paper surface, whereas methods without paper specifically determine reactivity of corrosive species towards copper surface. These tests are often considered to be complementary. In this work, method ADSTM D1275 B was applied in order to correlate standard methods with the reactivity study and corrosiveness ranking studies previously discussed. IEC 62535 method was not used to compare or confirm the results of this study because it implies the use of cellulose (Kraft paper), that can interfere in the corrosion reactions. ASTM D1275 B method was performed at 80°C, 100°C, 120°C, 150°C and 180°C.

Pictures reported in Figures S1-S2 (Supporting Information) clearly demonstrate that benzyl mercaptan is, among the studied compounds, the one more prone to form copper sulfide onto bare copper surfaces, even at low temperatures.

This result is in agreement both with the reactivity study and corrosiveness ranking previously discussed where, among mercaptans, benzyl mercaptan resulted to be the compound with the highest corrosion yield.

Also DBDS brings about a significant copper sulfide deposition on conductor, but this effect is evident only for temperatures higher than 150 °C, at least under the experimental conditions evaluated. This result supports, once again, that BMt attacks copper more strongly, and that, as mentioned above, corrosive effect of DBDS can be due to its conversion into BMt. For the other

mercaptans a clear corrosiveness can be established only at very high temperature (180 °C, except EtDt from 150 °C). The other important outcome produced by this investigation is the high corrosiveness showed by the three sulfoxides: beyond 150 °C, they cause an increasing black deposit, thus confirming their corrosive role highlighted by the TCS method. For the other investigated compounds, the assessment of a corrosiveness is tentative, because the observed colors can be subjectively interpreted (e.g.: DPDS and PVS).

CONCLUSIONS

This study allowed us to better understand the reactivity of several sulfur compounds, both in terms of stability under conditions of thermal and oxidative stress, and tendency to form copper sulfide in the presence of bare copper surfaces. Sulfur compounds belonging to different families (mercaptans, sulfides, disulfides, sulfoxides, thiophenes) showed different affinity against copper, and their reactivity scale is temperature-dependant. In fact, at relatively low temperatures (80 °C) mercaptans seem to be largely more corrosive than all other families of sulfur compounds. But, when temperature increases (up to 180 °C) we have observed an apparent inversion of reactivity scale, having disulfides and sulfoxides as the most corrosive families. This behavior, that cannot be explained only by considering the affinity of each compound against copper, or by the thermodynamic stability of the reaction by-products, may be caused by the concomitant presence of at least two different reactions: oxidative degradation and corrosive attack on copper. Both reactions involve all sulfur compounds, but the less thermally stable (i.e. mercaptans, as depicted by the reactivity study in this work), can be degraded at a rate faster than the corrosive reaction rate. This may explain the reason why method ASTM D1275 B is usually more sensitive to disulfides than to mercaptans: the applied temperature (150 °C) is high enough

to rapidly induce the oxidation of mercaptans before they can react with copper to an appreciable extent. On the other hand, disulfides exhibit a better resistance to oxidation at the test temperature, and the reaction of copper sulfide formation is dominant compared to the oxidative degradation. Other empirical tests (e.g. DIN 51353²⁷) are known to be more sensitive to mercaptans, and are also recommended by international standards^{12,28} to assess the corrosiveness of mineral oils. Their better response to mercaptans may be explained not only by the use of silver instead of copper as a reactive metal, but also by the lower applied temperature (100 °C), at which mercaptans are relatively thermally stable and can exhibit their corrosive tendency in an appreciable way, thus giving a visible color change in the test strip.

Our studies demonstrated that in case of thermally stable compounds, such as DBDS, the formation of copper sulfide increases with temperature.

Our research underlines the need for monitoring the presence of sulfoxides in mineral oil, especially in the case of free breathing units. As a matter of fact the oxidative deterioration of the oil may convert sulfides into corrosive sulfoxides, thus inducing an increased corrosiveness of the oil by effect of oil oxidation. It is worth mentioning the totally non-corrosive effect of dibenzothiophene.

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ASSOCIATED CONTENT

Supporting Information. Chemical structures of the sulfur compounds investigated. GC-AED conditions optimized for the quantification of sulfur compounds. Photographs of copper conductors after contact with each sulfur compound investigated according to the official method ASTM D1275B tested at different temperatures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Supporting Information for

Stability and reactivity of sulfur compounds against copper in insulating mineral oil: definition of a corrosiveness ranking

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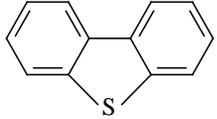
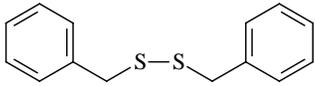
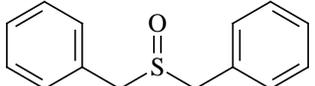
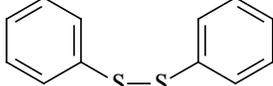
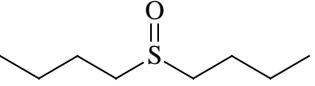
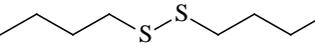
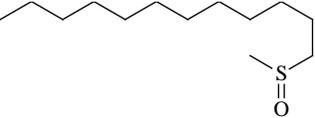
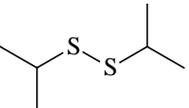
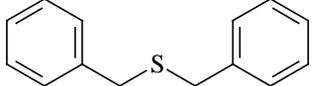
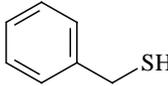
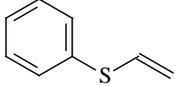
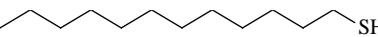
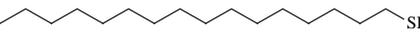
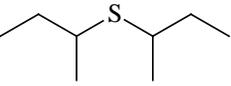
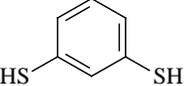
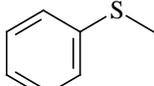
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Table S1: Sulfur compounds investigated. In *italic*: compounds found in transformer oils. In **bold**: species considered for the reactivity study as representative of their class.

Class	Structure	Name	Abbreviation	Class	Structure	Name	Abbreviation
Thiophenes		<i>Dibenzothio- phene</i>	<i>DBTf</i>	Disulfides		<i>Dibenzyl Disulfide</i>	<i>DBDS</i>
Sulfoxides		Dibenzyl Sulfoxide	DBSOx			Diphenyl Disulfide	DPDS
		Dibutyl Sulfoxide	DBuSOx			Butyl Disulfide	BuDS
		Dodecyl methyl sulfoxide	DcMeSOx		Isopropyl Disulfide	IPDS	
Sulfides		<i>Dibenzyl Sulfide</i>	<i>DBS</i>	Mercaptans		<i>Benzyl Mercaptan</i>	<i>BMt</i>
		Phenyl Vinyl Sulfide	PVS			Dodecyl Mercaptan	DCMt
		Pentamethylene Sulfide	PMeS			Hexadecyl Mercaptan	HDMt
		sec-Butyl Sulfide	sBS			Benzene-1,3-dithiol	BDT
		Thioanisole	TAS			Butyl Mercaptan	BuMt

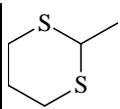
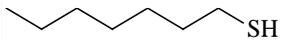
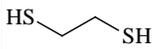
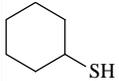
		2-Methyl-1,3-Dithiane	MeDT		  	Heptyl Mercaptan 1,2-Ethanedithiol Cyclohexanethiol	HeMt EtDt CET
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Table S2: GC-AED conditions optimized for the quantification of sulfur compounds.

Injector	Split type 300°C; 1 μ L; splitting ratio 1:10
Column	HP-1 Methyl Siloxane Capillary (100% PMSO) 60m \times 250 μ m \times 0,25 μ m
Carrier gas	He 6.0, 1 mL/min
Program temperature	0-2 min: 100°C
	3°C/min until 300°C
	300°C for 12 min
Detector conditions	Gas reagents: O ₂ , H ₂ Temperature of transfer line: 310 °C Cavity temperature: 310 °C λ = 181 nm (carbon spectral line)

Figures S1-S2. Photographs of copper conductors after contact with each sulphur compound investigated according to the official method ASTM D1275B tested at different temperatures

ASTM B	Temperatura di invecchiamento					
	80°C	100°C	120°C	140°C	160°C	180°C
DBS						
DBDS						
DPDS						
BuDS						
PVS						
BMt						
DCMt						
HDMt						
DBTf						
MeDT						
BDT						

Figure S2.

