

Received November 12, 2018, accepted December 17, 2018, date of publication December 19, 2018, date of current version January 11, 2019.

Digital Object Identifier 10.1109/ACCESS.2018.2888818

Protective Performance of Different Passivators on Oil-Paper Insulation Containing Multiple Corrosive Sulphides

HAOXI CONG^{ID}, MINHAO ZHANG, XIANG SHU, AND QINGMIN LI^{ID}, (Member, IEEE)

School of Electrical and Electronic Engineering, North China Electric Power University, Beijing 102206, China

Corresponding author: Haoxi Cong (conghaoxi@ncepu.edu.cn)

This work was supported in part by the National Natural Science Foundation of China under Grant 51807061 and in part by the Fundamental Research Funds for the Central Universities under Grant 2017MS005.

ABSTRACT The problem of sulfur corrosion has seriously affected the safe and stable operation of the power transformers. Currently, adding passivators into the transformer oil is the most effective method to suppress the problem. However, no explicit provisions have been made for the optimum concentration of the specific passivators. In this paper, the transformer oils with different corrosive sulfurs and different aging degrees were used to study the protective performance of three different passivators. By comparing the copper surface, the optimum concentrations for each passivators were acquired. Moreover, by testing the breakdown voltage, dielectric loss factor, volume resistivity, and moisture content of the insulating oil after adding passivators with the optimal concentration, the effect of three passivators on the oil quality was obtained. Results show that the three passivators have different protective performance on different types of corrosive sulfurs. Irgamet 39 has a better protective effect at lower concentrations than the other two. The protective effect of all three passivators on dodecyl mercaptan is poor, and a new type of passivator capable of protecting against dodecyl mercaptan needs to be developed. Moreover, the three passivators have different protection performance on the transformer oils with different aging degrees. The protective performance is poor especially for the oils with longer running years or passivators with lower concentrations. Among the three passivators, Irgamet 39 had the smallest impact on the oil quality, followed by T571 and then TTA. The above research can provide some references for guiding the passivator addition in actual projects and preventing the occurrence of sulfur corrosion failures.

INDEX TERMS Insulation oil, corrosive sulphides, passivator, optimum concentration, oil quality.

I. INTRODUCTION

The corrosive sulphides in the transformer oil could react with the copper wire to generate cuprous sulfide, which is deposited on the surface of the copper wires, leading to reduce its electrical properties and cause insulation failure [1], [2]. In recent decades, the corrosive sulfur faults have been substantially discovered in China, Japan, Europe, and other countries [3], [4]. Due to the lack of accurate risk assessment on sulfur corrosion and effective countermeasures, the insulation failure caused by sulfur corrosion has seriously affected the safe operation of power transformers.

At present, lots of methods have been done to reduce the damage of corrosive sulfur. For instance, strengthening the inspection of new transformer oil, controlling the operating conditions, oil change or oil mixing, desulfurization, and

addition of metal passivators. However, none of them can completely eliminate the phenomenon of sulfur corruptions. Among those methods, adding passivators into the transformer oil is the most useful method [5]. Ren *et al.* [6] have found that the passivator can produce a protective film on the copper winding surface, hindering the reaction of corrosive sulfur and copper windings. Lukic *et al.* [7] found that TTA could react with oxygen to suppress the precursor of Cu_2S , and also form the protective film on the surface of copper windings, which both can protect the copper winding from corrosion. Wan *et al.* [8], Sundara *et al.* [9] and other scholars have found that the corrosion inhibition of the Irgamet 39 copper winding is also a film-forming type and the protective film is very strong, which is resistant to high temperatures and oxygen, thus improving the oxidation stability and dielectric

loss factor of the sample oil. Martins and Gomes [10] found that when the concentration of Irgamet 39 in the oil is greater than 50 ppm, it can have a good corrosion inhibition effect and also improve the oxidation stability of the oil sample and reduce the sediment. Wan *et al.* [11] and Qian *et al.* [12] and others found that T551 can effectively reduce the copper content of transformer oil, which has a significant inhibitory effect on copper corrosion and oil aging. Yu *et al.* [13] found that the small transformers with paper-wrapped copper winding can impede the copper corrosion and passivate the metals, weakening their ability to promote oil oxidation and increasing the antioxidant properties of oil. Ingvild *et al.* [14] found that no effect of Irgamet 39 on the corrosion of copper in systems had started and the effect was found to be very good on fresh copper surfaces. Moreover, the factors such as temperature, copper, insulating paper and atmospheric environment all have effects on the dissipation characteristics of the passivators. For instance, the presence of oxygen would lead to a large consumption of passivators [15]. Arvidsson and Ravnemyhr [16] pointed out that a slight increase of temperature would lead to the rapid consumption of passivators. The IEC 60422-2013 stipulates adding passivator with mass fraction greater than 10^{-4} in the transformer oil and maintaining the mass fraction greater than 50×10^{-6} to ensure the safe operation of the transformer. However, no explicit regulations are given for the optimum concentration of the specific passivators. Though adding passivators to the transformer oil to retard the sulfur corrosion has been verified, the exact concentration of passivators, especially the difference of protection effectiveness between operating oils and new oils still need to be further explained.

In this paper, the dibenzyl disulfide (DBDS), dodecanethiol (DDM) and a combination of the two were added to the non-corrosive transformer oil, and with addition of three different concentrations of Irgamet 39, T571 and TTA. Then the accelerating thermal aging test were conducted at 150 °C temperature. The corrosion degree of the copper surface was observed to acquire the optimal concentration of each passivator for different corrosive sulfurs. By testing the breakdown voltage, dielectric loss factor, volume resistivity and moisture content of the insulating oil after adding the optimal concentration of the passivators, the effect of three passivators on the oil quality was obtained.

II. OIL-PAPER INSULATION AGING EXPERIMENT ON MULTIPLE CORROSIVE SULFIDES

The test materials were: non-corrosive new transformer oil, operating oil of Fujian Shuikou substation, insulation paper (thickness 0.07 mm, width 25 mm), copper windings, TTA, Irgamet 39 and T571 passivators. The molecular structure of TTA is $C_7H_7N_3$. The molecular structure of Irgamet 39 and T571 are both $C_{24}H_{42}N_4$, except that T571 is added with a small amount of antioxidant. The concentration addition of sulfide and passivators are shown in Table 1. For the protection mechanism of the above three passivators, what TTA and Irgamet 39 have in common is that they can be

TABLE 1. Concentration addition of sulfide and passivators.

Group of sulfide addition	Type of passivators	Content of passivator Oppm
A: DBDS(200ppm)	Irgamet 39	50ppm
B: DDM(400ppm)	TTA	100ppm
C: DBDS+DDM(100+200ppm)	T571	150ppm
D: Shuikou oil		200ppm

adsorbed on the copper surface to form a protective film, which can prevent the corrosive sulfides from reacting with the copper windings. The differences are as follows. On one hand, TTA could react with oxygen and Cu^+ to inhibit the precursor required for the formation of Cu_2S , which Irgamet 39 does not have. On the other hand, the protective film formed by Irgamet 39 on the copper windings is very strong and resistant to high temperatures or oxidization, which TTA does not have [17]. T571 is a passivator made up of Irgamet 39 and a small amount of antioxidants, therefore its purity is lower than Irgamet 39 [8].

At present, there are some qualitative test methods and few quantitative test methods for sulfur corrosion. The qualitative test of sulfur corrosion can evaluate whether the insulating oil is corrosive, such as the standards DIN 51353, ASTM D1275 and ISO 5662. The qualitative test could also judge the corrosion degrees in a certain quantitative extent, such as the standard ASTM D 130/IP 154. On the other hand, there are few studies on the quantitative evaluation of sulfur corrosion, as it is a difficult point and there always occurs that the sulfur concentration is lower than the detection line. On the whole, the method for accurately evaluating the sulfur corrosion of transformer oil is still based on qualitative tests. Due to the problem of detection lines, only few immature quantitative evaluation schemes have been developed. Therefore, the mature ASTM D 130/IP 154 method was finally selected to evaluate the corrosive degree of sulfur corrosion in this paper.

The specific experimental steps are as follows. Firstly, the copper strip wrapped of insulating paper was cut to the 3 cm preliminary test sample by the bolt cutter. The outer layer of the insulation paper was peeled off with tweezers, leaving only the innermost layer of insulating paper as the test copper strap wire. Then the 15 mL pre-treated insulating oil samples (shown in Table 1) were added to the new 20 mL empty bottle and the prepared 3 cm test copper strap wire was placed upright into the empty bottle with tweezers. After ensuring that the test copper strap wire is completely immersed into the oil sample, the bottleneck of bottles were sealed by a metal cap made of rubber gasket, as shown in Figure 1. All sample bottles were put into a thermostat with temperature controlled at $150 \text{ }^\circ\text{C} \pm 2 \text{ }^\circ\text{C}$. After aging for $72 \text{ h} \pm 0.5 \text{ h}$, the sample bottles were taken out with a cap opener. After cooling to the ambient temperature, the copper strip was removed from the bottles and rinsed with petroleum ether to remove the oil

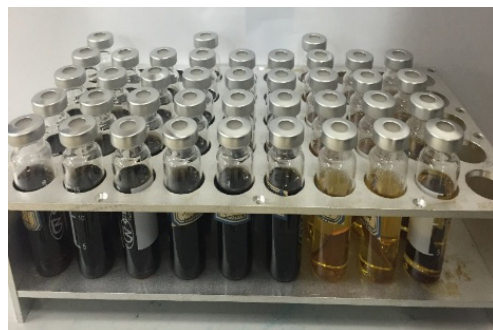


FIGURE 1. The oil samples with different concentration of sulfides and passivators.

stains on the insulating paper and copper strips. Then copper strips were dried for 5 minutes to observe the corrosion degree of its surface.

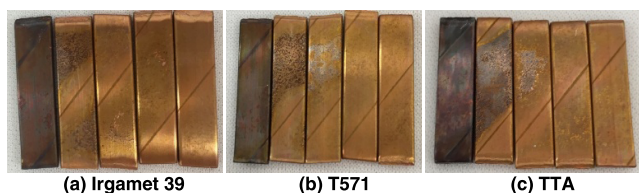


FIGURE 2. Specimen copper surface color of Group A (DBDS). (a) Irgamet 39. (b) T571. (c) TTA.

TABLE 2. Specimen copper corrosive degrees of Group A (DBDS).

Passivator	Passivator concentration (mg/L)				
	0	50	100	150	200
Irgamet 39		3a	2e-3a	2e	2d
T571	3b-4a	3a	3a	2d	2d
TTA		3b	3a	2e	2d

The surface color of copper strips in group A is shown in Figure 2. The passivators shown in Figure 2 (a), (b), and (c) are Irgamet 39, T571 and TTA, respectively. The concentrations of the passivators from left to right in each figure were 0 mg/L, 50 mg/L, 100 mg/L, 150 mg/L and 200 mg/L. The copper corrosive degrees of group A is shown in Table 2. According to the corrosive degrees of the copper surface, it can be judged that full protection of DBDS can be achieved at 200 mg/L for the three passivators. After reaching a certain concentration, the protective effect no longer becomes better with the increase of concentration. The concentration at this time is defined as the best concentration. In addition, the best concentration for Irgamet 39 is 200 mg/L, the best concentration for T571 is 150 mg/L and the best concentration for TTA is 200 mg/L. On the whole, Irgamet 39 has the best protective effect at low concentrations, followed by T571 and TTA.

The surface color of copper strips in group B is shown in Figure 3. The passivators shown in Figure 3 (a), (b) and (c)

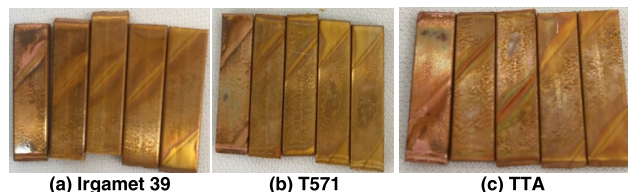


FIGURE 3. Specimen copper surface color of Group B (DDM). (a) Irgamet 39. (b) T571. (c) TTA.

TABLE 3. Specimen copper corrosive degrees of Group B (DDM).

Passivator	Passivator concentration (mg/L)				
	0	50	100	150	200
Irgamet 39		3a-3b	2e	2e	2e
T571	3a-3b	3a	3a	3a	2e
TTA		3a-3b	3a-3b	3a	3a

are also Irgamet 39, T571 and TTA, respectively. The concentrations of passivators from left to right were 0 mg/L, 50 mg/L, 100 mg/L, 150 mg/L, and 200 mg/L. The copper corrosive degrees of group B is shown in Table 3. As can be seen from the table, though the corrosion degree in the DDM group is lower than the DBDS group, the three passivators cannot completely protect the mercaptan. Briefly, the Irgamet 39 group has relatively good protective effect. The best concentration for Irgamet 39 is 100 mg/L, the best concentration for T571 is 200 mg/L, and the best concentration for TTA is 150 mg/L.

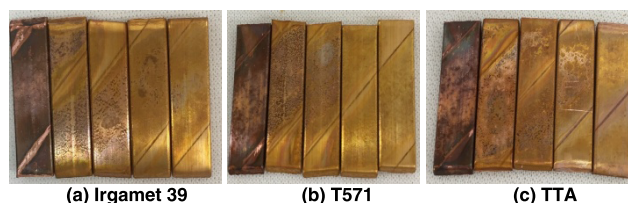


FIGURE 4. Specimen copper surface color of Group C (DBDS+DDM). (a) Irgamet 39. (b) T571. (c) TTA.

The surface color of copper strips in group C is shown in Figure 4, and the passivators shown in Figures 4 (a), (b) and (c) are Irgamet 39, T571 and TTA, respectively. The concentrations of passivators added from left to right were 0 mg/L, 50 mg/L, 100 mg/L, 150 mg/L, and 200 mg/L. The copper corrosive degrees of group C is shown in Table 4. According to the corrosion degree of the copper surface, it can be judged that the three passivators cannot fully protect DBDS and DDM at the same sulfur concentration, which may be due to the presence of mercaptan. The corrosion effect of two sulfide superposition is greater than that of any single corrosion action. The protective effect of T571 is relatively better. After the two kinds of corrosive sulfur are mixed, the protective effect of the passivators at a low concentration are all reduced. Moreover, the reduction

TABLE 4. Specimen copper corrosive degrees of Group C (DBDS+DDM).














Passivator	Passivator concentration (mg/L)				
	0	50	100	150	200
Irgamet 39		3a	3a	2d	2d
T571	4a-4b	3b	3a	3a	2d
TTA		3a	3a	2e	2d

degree of T571 is small and the protective effect is better. By comparison, the best concentration for Irgamet 39 is 150 mg/L, the best concentration for T571 is 200 mg/L and the best concentration for TTA is 200 mg/L.

For the above three groups, the protective effect of TTA is worse than the previous two. On one hand, TTA reacts with oxygen and Cu⁺ to inhibit the lead material required for the formation of Cu₂S. The chemical reaction needs to be carried out at a suitable temperature, and the high temperature of 150 °C used in the experiment may inhibit the chemical reaction. The protective film produced by Irgamet 39 is resistant to high temperatures, so TTA is not as protective as Irgamet 39. On the other hand, as TTA is less soluble in the insulating oils, the actual concentration dissolved in the oil is much lower than the added concentration.

The surface color of the copper strips in group D is shown in Table 5. It can be seen that at the same temperature and aging time, the copper strips with Irgamet 39 of

TABLE 5. Specimen copper surface color and corrosive degrees of Group D.

Passivator Concentration	Irgamet 39	T571	TTA	Blank group
50 mg/L	 3a	 3a	 1b	
100 mg/L	 3a	 3a	 1b	
150 mg/L	 2d	 2c	 1b	
200 mg/L	 2d	 2c	 1b	

50 mg/L or 100 mg/L have appeared corrosion, though the corrosion degree is lower than the blank group. In the T571 group, there are different corrosion degrees in the four concentrations, and the corrosion degree is also lower than the blank group. However, TTA has the best protection effect. Under the four concentrations, the copper sheet shows a pale yellow color with no corrosion.

The reason for the above difference in protective effect is that Irgamet 39, T571, and TTA are all nitrogen-based passivators. In the insulating oil, there are lone pair electrons existed in the heteroatom N atoms of the passivator, which are easily combined with the *d*-orbitals of the metal to form a coordination bond. Then the metal *d*-orbitals will provide electrons to the heteroatoms to form a feedback coordination bond, thereby forming a polymer-like protective film on the metal surface. As can be seen from the above experiment, the protective effect of Irgamet 39 and T571 is not much different in several sets of oil samples. The protective effect of TTA is better than the previous two. This may be due to the produced acid during the long-term operation of the oil samples, which leads to an increase on the acid number and a decrease on the pH value of the oil samples [18]. The effect of Irgamet 39 and T571 is closely related to the pH values. When they are in a strong acidic environment, Irgamet 39 and T571 produce the protective film faster, which results that the film has a lower compactness and adsorption with copper [17]. Hence, for the operating oil samples, Irgamet 39 and T571 are not as protective as TTA. The best protection concentration for Irgamet 39 is 150 mg/L, the best protection concentration for T571 is 150 mg/L, and the best protection concentration for TTA is 50 mg/L.

III. EFFECT ON THE OIL QUALITY WITH PASSIVATORS AT THE OPTIMAL CONCENTRATION

Based on the above studies, the optimal concentrations for three passivators were obtained. Then each group of samples were added with the optimal concentration (shown in Table 6) and fully stirred at 40 °C to ensure that the passivators were fully dissolved in the oil. The characteristic parameters of the insulating oil were tested as follows. The breakdown voltage was referred to GB/T 507-2002 standard “Insulating liquids-Determination of the breakdown voltage at power frequency”. The oil moisture content was refer to GB/T

TABLE 6. Optimal concentration for different passivators with different sulfides.

Type of sulfide	Irgamet 39 (mg/L)	T571 (mg/L)	TTA (mg/L)
DBDS(200ppm)	200	150	200
DDM(400ppm)	100	150	200
DBDS+DDM (100+200ppm)	150	200	200
Shuikou oil	150	150	50

26793-2011 standard “Coulometry micro water teller” and ASTM D1533-2000 standard “Standard Test Method for Water in Insulating Liquids by Coulometric Karl Fischer Titration”. The volume resistivity and dielectric loss factor was referred to GB/T 5654-1985 standard “Measurement of relative permittivity, dielectric dissipation factor at power frequency and volume resistivity of insulating liquids”.

The test results on the breakdown voltage of each group oil samples are shown in Figure 5. As can be seen from the figure, the breakdown voltage is slightly increased except for the TTA group. It is due to that the adding passivator of Irgamet 39 and T571 will be adsorbed on the surface of the copper electrode to form a multilayer protective film, blocking the emission of electrons and the formation of streamers. However, as TTA is hardly soluble in oil, it is equivalent to an impurity after addition, resulting in easier breakdown.

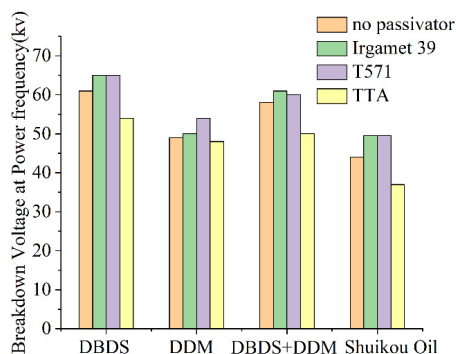


FIGURE 5. The breakdown voltage of oil samples at power frequency.

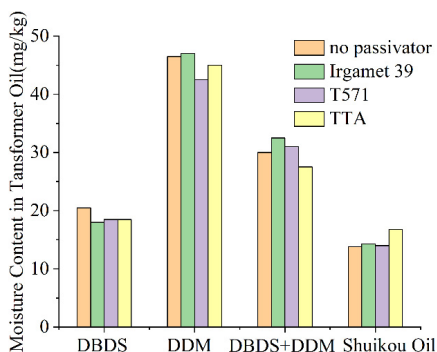


FIGURE 6. The moisture test results of oil samples.

The moisture test results of the sample oils are shown in Figure 6. From the figure, it can be seen that the oil contents of the oil samples are different. This is related to the respective water absorption of the different sulfides. However, after the addition of passivators, the moisture content did not change much.

The volume resistivity test results of the insulating oil samples are shown in Figure 7. As can be seen from the Figure, after the addition of TTA, it will cause decrease on the volume resistivity of the oil sample. However, when the

volume resistivity of the oil sample is high, Irgamet 39 and T571 will lead to a decrease on the volume resistivity. On the contrary, when the volume resistivity of the oil sample is low, the addition of Irgamet 39 and T571 may lead to an increase on the volume resistivity. Among them, the addition of T571 is the most obvious phenomenon. However, TTA will always cause a decrease on the volume resistivity. This is because the poor solubility of TTA leads to an increase of impurities in the oil and then a decrease on the volume resistivity.

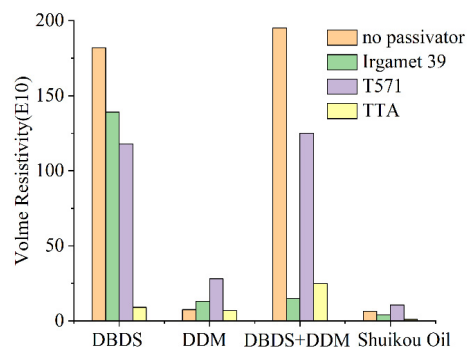


FIGURE 7. The volume resistivity test results of oil samples.

The dielectric loss factor test results of insulating samples are shown in Figure 8. From the figure, it can be seen that the addition of TTA will cause a significant increase on the dielectric loss factor of the oil sample. The addition of Irgamet 39 will also result in dielectric loss factor of the oil sample, while the addition of T571 could reduce the dielectric loss factor. As is known, the dielectric loss of insulating oil includes the conductance loss and the polarization loss. Under the action of the electric field, the polar substances will change with the change of the electric field direction. The above process would cause part of the electrical energy converted into thermal energy loss, thus increasing the dielectric loss factor. Because of the poor solubility of TTA, its addition is equivalent to more polar impurities, leading to a significant increase on dielectric loss. According to the previous analysis, the addition of T571 may lead to an increase on volume resistivity, causing a decrease on conductance and dielectric loss.

IV. PROTECTION EFFECT OF PASSIVATOR ON INSULATING OIL WITH DIFFERENT AGING DEGREE

The test materials include new transformer oil without corrosive sulfur, DBDS, DDM, Irgamet 39, T571, TTA and flat copper wire wrapped of insulating paper. The 200 mg/kg DDM and 100 mg/kg DBDS were added into the new transformer oil, which was then degassed and dehydrated at 40 °C /50 Pa for 24 hours. The pre-treated oil sample was placed in an aging chamber at 130 °C for accelerated thermal aging, and aged oil samples with aging time of 4 days, 8 days, and 12 days were obtained. According to the 6 °C

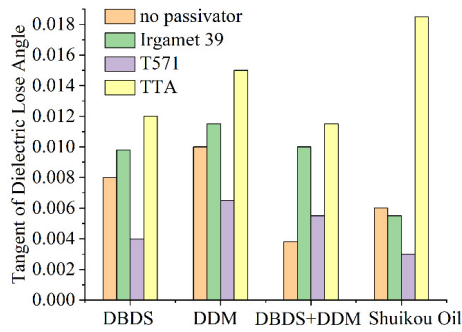


FIGURE 8. The dielectric loss factor test results of oil samples.

principle proposed by the international electrotechnical commission (IEC), the above-mentioned insulation oil samples aged for 4 days, 8 days, and 12 days are corresponding to the insulation oil samples for 3.52 years, 7.04 years, and 10.56 years under normal conditions, as shown in Figure 9.



FIGURE 9. The insulation oils with different aging time.

The 3 cm test samples were cut by bolt cutter from a flat copper wire wrapped with insulating paper. Then the different concentrations of Irgamet 39, T571 and TTA (0 mg/kg, 50 mg/kg, 100 mg/kg, 150 mg/kg and 200 mg/kg) were added to each group of samples. The metal caps with the rubber seal were sealed at the head with a capping pliers. All the prepared sample bottle were put into a thermostatic chamber where temperature were controlled at $150\text{ }^{\circ}\text{C}\pm 2\text{ }^{\circ}\text{C}$. The aging time is 72 h. The best concentration of passivator was judged according to the degree of copper corrosion by reference to the standard ASTM D 130/IP 154.

The protective effect of Irgamet 39 on insulation oil samples with different degrees of aging time is shown

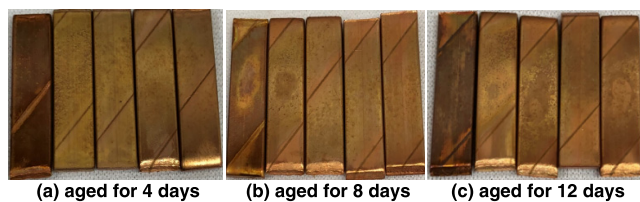


FIGURE 10. Protective effect of Irgamet 39 with different concentrations. (a) Aged for 4 days. (b) Aged for 8 days. (c) Aged for 12 days.

TABLE 7. Copper corrosive degrees of Irgamet 39 with different concentration.

Aging time	Passivator concentration of Irgamet 39 (mg/L)				
	0	50	100	150	200
4 days	3a-3b	2e	2d	2d	2d
8 days	3b	2e-3a	2d	2d	2d
12 days	3b-4a	3a-3b	3a-3b	3a	2e

in Figure 10. The insulating oil samples aged for 4 days, 8 days and 12 days are shown in Fig. 10 (a), (b) and (c), respectively. The copper sheets from left to right were with passivator concentrations of 0 mg/kg, 50 mg/kg, 100 mg/kg, 150 mg/kg and 200 mg/kg. By Comparing Fig. 10(a), (b) and (c), it can be seen that when the sulfide concentration is same, the higher the aging degree of the insulation oil sample, then the higher corrosion degree of the copper sheet. In addition, the protective effect at the same passivator concentration is also decreased with the aging time increases. The decline of this protective effect is especially obvious for low concentration passivator. It can be seen that as the aging time of the sample increases, a higher concentration of passivator is required to achieve complete protection against corrosion, which may be related to the acid value in the oil. As the aging time of the oil sample increases, the acid value in the oil increases [10], and the generated acid may destroy the protective film formed on the surface of the copper windings by the passivator. Therefore, for samples with a longer aging time, a higher concentration of passivator is required to achieve complete protection against corrosion. According to Fig. 10(a), samples added 100 mg/kg of passivator show the best protective effect among samples aged for 4 days. According to Fig. 10(b), samples added 100 mg/kg of passivator show the best protective effect among samples aged for 8 days. According to Fig. 10(c), samples added 200 mg/kg of passivator show the best protective effect among samples aged for 12 days.

The protective effect of T571 on insulation oil samples with different degrees of aging time is shown in Figure 11. The insulating oil samples aged for 4 days, 8 days and 12 days are shown in Fig. 11 (a), (b) and (c). The copper sheets from left to right were with passivator concentrations of 0 mg/kg, 50 mg/kg, 100 mg/kg, 150 mg/kg and 200 mg/kg. Comparing with Figure 6, it can be seen that the protective effects of the T571 are similar to Irgamet 39, as the ingredients are roughly the same. Also, the protective effect at the same passivator concentration is also decreased with the aging time increases. According to Fig. 11(a), samples added 50 mg/kg of passivator show the best protective effect among samples aged for 4 days. According to Fig. 11(b), samples added 100 mg/kg of passivator show the best protective effect among samples aged for 8 days. According to Fig. 11(c), samples added 50 mg/kg of passivator show the best protective effect among samples aged for 12 days.

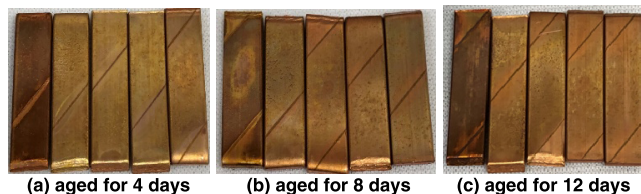


FIGURE 11. Protective effect of T571 with different concentrations. (a) Aged for 4 days. (b) Aged for 8 days. (c) Aged for 12 days.

TABLE 8. Copper corrosive degrees of T571 with different concentration.

Aging time	Passivator concentration of T571 (mg/L)				
	0	50	100	150	200
4 days	3a-3b	2d	2d	2d	2d
8 days	3b	3a	2e	2e	2e
12 days	4a	2e-3a	2e-3a	2e-3a	2e-3a

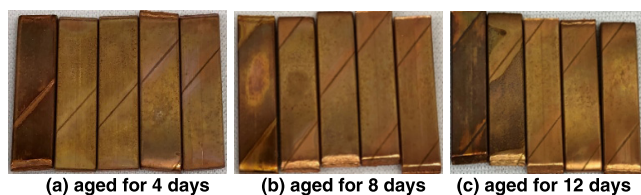


FIGURE 12. Protective effect of TTA with different concentrations. (a) Aged for 4 days. (b) Aged for 8 days. (c) Aged for 12 days.

TABLE 9. Copper corrosive degrees of TTA with different concentration.

Aging time	Passivator concentration of TTA (mg/L)				
	0	50	100	150	200
4 days	3a-3b	2e	2e	2e	2d
8 days	3b	2e-3a	2d	2d	2d
12 days	4a	3b-4a	2e	2d	2d

The protective effect of TTA on insulation oil samples with different degrees of aging time is shown in Figure 12. The insulating oil samples aged for 4 days, 8 days and 12 days are shown in Fig. 12(a), (b) and (c). The copper sheets from left to right were with passivator concentrations of 0 mg/kg, 50 mg/kg, 100 mg/kg, 150 mg/kg and 200 mg/kg. As can be seen from the figure, the protective effect at the same passivator concentration is also decreased with the aging time increases. According to Fig. 12 (a), samples added 200 mg/kg of passivator show the best protective effect among samples aged for 4 days. According to Fig. 12(b), samples added 100 mg/kg of passivator show the best protective effect among samples aged for 8 days. According to Fig. 12(c), samples added 150 mg/kg of passivator show the best protective effect among samples aged for 12 days.

Combining the above research on the oil quality of the passivators, it is known that TTA has the greatest influence on the oil quality, as it is hardly soluble in the

insulating oil. Therefore, for the insulation oil with running time of about 3.5 years, it is recommended to add 100 mg/kg Irgamet 39 or 50 mg/kg T571. For the insulation oil with running time of about 7 years, it is recommended to add 100 mg/kg Irgamet 39 or 100 mg/kg T571. For the insulation oil with running time of about 10 years, it is recommended to add 200 mg/kg Irgamet 39 or 50 mg/kg T571. For the insulation oil with longer operating years, the passivators have poor protection effect at low concentration, thus it is necessary to pay attention to the content of passivators and maintain it at a relatively high level in the insulation oil.

V. CONCLUSION

The corrosive sulfurs of DBDS, DDM and the combination of two were added to the non-corrosive transformer oil, and with different passivator concentrations of Irgamet 39, T571 and TTA. The accelerated thermal aging test was carried out with different sulfurs and different aging degree. The corrosive extent of copper surface were observed to obtain the best concentration of passivators for different sulfurs, the main results are as follows.

(1) The passivators have different protection on different corrosive sulfur. For the protection against DBDS, all three kinds of passivator have good effect. However, the TTA is hardly soluble in the insulating oil, while the effect of Irgamet 39 and T571 on the quality of oil is small. The protection of Irgamet 39 is best when reducing the passivator concentration to a lower level, and Irgamet 39 of 200 mg/kg is considered to be the best choice. For the protection of DDM, the effect of the three passivator is general, and the protection effect of Irgamet 39 is relatively better. Considering the effect on the quality of the oil, choosing the T571 of 200 mg/kg is more appropriate. For the protection against of DBDS and DDM, T571 is the best of the three passivators, Irgamet 39 is the second, and TTA is the worst. Considering the impact on oil quality, it is more appropriate to choose 200 mg/kg T571.

(2) The passivators have different protection effect on insulation oil samples with different degrees of aging time. For the transformer oil with a running time of about 3.5 years, it is recommended to add 100 mg/kg Irgamet 39 or 50 mg/kg T571. For transformer oil with a running time of about 7 years, it is recommended to add 100 mg/kg Irgamet 39 or 100 mg/kg T571. For transformer oil with a running time of about 10 years, it is recommended to add 200 mg/kg Irgamet 39 or 50 mg/kg T571. For transformer oil with longer running time (or higher aging degree), the protective effect on oil is poor at low concentration. Therefore, attention should be paid to the content of the passivator and maintain the content of passivator in the oil in a high level.

REFERENCES

[1] M. Dahlund *et al.*, "Copper sulphide in transformer insulation," CIGRE WG A2-32, Paris, France, Final Rep. Brochure 378, 2009.
 [2] L. Yang, S. Gao, B. Deng, and Z. Cheng, "Corrosion mechanisms for electrical fields leading to the acceleration of copper sulfide deposition on insulation windings," *Ind. Eng. Chem. Res.*, vol. 56, pp. 9124-9134, Jul. 2017.

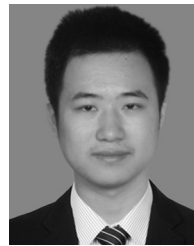
- [3] S. D. Flora, Thirumurthy, K. P. Meena, and J. S. Rajan, "Experimental simulation of effects of high temperatures on paper oil insulation of transformers in presence of DBDS in mineral oil," *IEEE Trans. Dielectr. Electr. Insul.*, vol. 24, no. 5, pp. 2819–2827, Oct. 2017.
- [4] S. Ren, L. Zhong, Q. Yu, X. Cao, and S. Li, "Influence of the atmosphere on the reaction of dibenzyl disulfide with copper in mineral insulation oil," *IEEE Trans. Dielectrics Electr. Insul.*, vol. 19, no. 3, pp. 849–854, Jun. 2012.
- [5] J. Nunes, "The copper corrosion phenomenon," Nynas Naphthenics, Stockholm, Sweden, Tech. Rep. 5, 2007.
- [6] S.-Z. Ren, L.-S. Zhong, and X.-L. Cao, "Research on the corrosive sulfur in mineral insulation oils," *Insulating Mater.*, vol. 43, pp. 69–73, Mar. 2010.
- [7] J. M. Lukic, S. B. Milosavljevic, and A. M. Orlovic, "Degradation of the insulating system of power transformers by copper sulfide deposition: Influence of oil oxidation and presence of metal passivator," *Ind. Eng. Chem. Res.*, vol. 49, pp. 9600–9608, Sep. 2010.
- [8] T. Wan, H. Qian, Z. Zhou, S. K. Gong, X. Hu, and B. Feng, "Suppressive mechanism of the passivator irgamet 39 on the corrosion of copper conductors in transformers," *IEEE Trans. Dielectr. Electr. Insul.*, vol. 19, no. 2, pp. 454–459, Apr. 2012.
- [9] J. S. Rajan, C. J. Naidu, and K. Dwarakanath, "Influence of metal passivator on the corrosion of copper conductors due to sulphur in oil," in *Proc. IEEE Int. Symp. Elect. Insulating Mater.*, Sep. 2008, pp. 487–490.
- [10] M. A. G. Martins and A. R. Gomes, "Experimental study of the role played by dibenzyl disulfide on insulating oil corrosivity-effect of passivator irgamet 39," *IEEE Elect. Insul. Mag.*, vol. 26, no. 4, pp. 27–32, Jul./Aug. 2010.
- [11] T. Wan, H. Qian, and S. Xu, "Study on the inhibition of copper corrosion with metal passivator T551 in transformer oil," *Petroleum Process. Petrochem.*, vol. 43, pp. 69–72, Nov. 2012.
- [12] H. Qian, Y. Ou, and X. Hu, "Treatment for Cu content abnormality in transformer oil by adding metal deactivator," *Hunan Electr. Power*, vol. 29, pp. 13–16, Jun. 2009.
- [13] H.-M. Yu, S.-J. Ma, Y.-C. Meng, Q. Zhang, L.-J. Zhang, and C.-M. Guo, "Research on transformer sulfur corrosive inhibition with metal passivator," *Transformer*, vol. 48, pp. 37–42, Feb. 2011.
- [14] I. Tronstad, C. M. Roel, W. R. Glomm, E. A. Blekkan, and M.-H. G. Ese, "Ageing and corrosion of paper insulated copper windings: The effect of irgamet 39 in aged insulated oil," *IEEE Trans. Dielectr. Electr. Insul.*, vol. 22, no. 1, pp. 345–358, Feb. 2015.
- [15] Y. Zhao, Y. Qian, W. Su, Y. Li, L. Zhong, and Q. Yu, "Inhibition effectiveness and depletion characteristic of Irgamet 39 in transformer oil," *IEEE Trans. Dielectr. Electr. Insul.*, vol. 23, no. 6, pp. 3382–3388, Dec. 2017.
- [16] L. Arvidsson and E. Ravnemyhr, "Laboratory study: Mitigation of sulphidation attacks on copper by use of a Benzo-Tri-Azole derivative," in *Proc. IEEE Elect. Insul. Conf.*, Jun. 2016, pp. 414–418.
- [17] J. L. Song, W. G. Chen, L. L. Dong, J. J. Wang, and N. Deng, "An electroless plating and planetary ball milling process for mechanical properties enhancement of bulk CNTs/Cu composites," *J. Alloys Compounds*, vol. 720, pp. 54–62, Oct. 2017.
- [18] R.-J. Liao, E.-D. Hu, L.-J. Yang, and Z.-M. Xu, "The investigation on thermal aging characteristics of oil-paper insulation in bushing," *J. Electr. Eng. Technol.*, vol. 10, pp. 1114–1123, May 2015.



HAOXI CONG was born in Weifang, Shandong, China. He received the B.S. degree in electrical engineering and the Ph.D. degree in high voltage and insulation from Shandong University, Jinan, China, in 2011 and 2016, respectively. He is currently a Lecturer with the School of Electric and Electronic Engineering, North China Electric Power University. His current research interests include condition monitoring of high-voltage power apparatus.



MINHAO ZHANG received the B.Sc. degree (Hons.) in electrical engineering from North China Electric Power University, China, in 2016, where she is currently pursuing the M.Sc. degree, with a specific research interest in condition monitoring of high-voltage power apparatus.



XIANG SHU received the B.Sc. degree in electrical engineering from North China Electric Power University, China, in 2015, where she is currently pursuing the M.Sc. degree, with a specific research interest in condition monitoring of high-voltage power apparatus.



QINGMIN LI (M'07) received the B.Sc., M.Sc., and Ph.D. degrees from Tsinghua University, China, in 1991, 1994, and 1999, respectively, all in electrical engineering. In 1996, he joined Tsinghua University as a lecturer. In 2000, he came to U.K. as a Postdoctoral Research Fellow with Liverpool University and then with Strathclyde University. In 2003, he joined Shandong University, where he was a Professor in electrical engineering until 2011. He was also with Arizona State University,

USA, as a Visiting Professor, in 2010. He is currently a Professor in electrical engineering with North China Electric Power University, China. His current research interests include high-voltage engineering, applied electromagnetics, condition monitoring and fault diagnostics, and high-voltage power electronics. He is a member of IET.

...