Influence of copper on the by-products of different oil-paper insulations

Jian Hao¹,², Ruijin Liao¹, George Chen² and Chao Ma³
¹ The State Key Laboratory of Power Transmission Equipment & System Security and New Technology, Chongqing University, China
² School of Electronics and Computer Science, University of Southampton, UK
³ Gansu Electric Power Research Institute, China

E-mail: cquhaojian@126.com

Abstract. Transformer failure caused by the corrosion of copper material in transformer attracts great attention of researchers and engineers. In this paper, Karamay No. 25 naphthenic mineral oil, Karamay No. 25 paraffinic mineral oil, Kraft paper and copper were used to compose four combinations of oil-paper insulation samples. The ageing by-products and dielectric properties of the four combinations of oil-paper insulation samples were compared after they were thermally aged at 130°C. The influence of copper on the by-products and dielectric properties of different oil-paper insulations was obtained. The results show that copper can accelerate the ageing rate of insulation oils and reduce their AC breakdown voltage. The content of copper substance dissolved in insulating oil increases with ageing time at first and then decreases. The paper aged in the oil-paper insulation sample with copper has higher moisture content than the one without copper. Results of energy dispersive spectroscopy (EDS) in the scanning electron microscope (SEM) show that there is copper product deposited on the surface of insulation paper. The insulation oil and paper aged in the oil-paper insulation sample with copper have higher dielectric loss and conductivity than that without copper.

1. Introduction
Transformers play an important role in providing a reliable and efficient electricity supply and are one of the most critical equipments in electric power transmission and distribution systems. The insulation system in most power transformers consists of oil/paper on the copper windings, and there are also several oil-impregnated pressboard barriers between the high and low voltage windings, and sometimes also between windings and the core [1]. Copper has stable physico-chemical properties, low electrical resistivity and is widely used in power transformers [2]. At present, there are many investigations about the corrosive sulphur compounds present/formed in the insulating oil reacted with the copper windings and other copper parts [3-11], research on the influence of copper corrosion on the ageing characteristics of oil-paper insulation during its ageing process is limited.

In this paper, accelerated thermal ageing experiment of four different combination oil-paper insulation samples at 130°C, where observations on naphthenic oil-paper insulation and paraffinic oil-paper insulation samples both with and without copper were compared, respectively. Oil parameter includes the oil acidity, AC breakdown voltage and the copper substance content in the oils. Paper parameter has been carried out including paper colour, SEM and the moisture content of paper. At last, the influence of copper on the dielectric properties of oil-paper insulation sample was also provided.

Published under licence by IOP Publishing Ltd
2. Experiments
The test materials are common Kraft paper, Karamay No. 25 naphthenic mineral oil, Karamay No. 25 paraffinic mineral oil and rectangular copper. Insulating oil used in the experiment was provided by China Chongqing Chuan Run Co. Ltd. The parameters of naphthenic oil and paraffinic oil meeting the specifications of IEC 60296 are presented in Table 1. The abbreviations of four combination oil-paper insulation samples are presented in Table 2. Rectangular copper strips, whose dimensions were 5 mm in width, 7.5 mm in length and 0.2 mm in thickness, were used. They were polished with sand paper firstly to obtain active surfaces. After polishing, the strips were immersed in naphthenic oil and paraffinic oil respectively to avoid the oxidation of surface. Kraft paper, whose dimensions were 5 mm in width and 0.07 mm in thickness, were wrapped five turns around the strip and then the bundle was bound with cord.

Table 1. Typical parameters of naphthenic and paraffinic oil

| Property                        | Naphthenic oil | Paraffinic oil |
|---------------------------------|----------------|----------------|
| Density at 20°C (kg/m³)         | 882.9          | 872.8          |
| Kinematic viscosity 40°C (mm²/s)| 9.655          | 10.06          |
| Pour point (°C)                 | -45            | -24            |
| Flash point (°C)                | 140            | 159            |
| Acidity (mg KOH/g)              | 0.01           | 0.022          |
| Breakdown voltage (2.5mm gap electrodes) (kV) | 55            | 42             |
| Corrosive sulphur               | non-corrosive  | non-corrosive  |

Table 2. Samples used for thermal ageing test

| Sample name | Sample composition                          |
|-------------|---------------------------------------------|
| NK          | naphthenic oil + Kraft paper                |
| NKC         | naphthenic oil + Kraft paper + copper       |
| PK          | paraffinic oil + Kraft paper                |
| PKC         | paraffinic oil + Kraft paper + copper       |

Figure 1. Pre-treatment of samples and the flow chart of ageing test

The pre-treatment of samples and the flow chart of ageing were shown in Figure 1. After being pre-treated, the moisture content of paper is 0.70%. The oil samples have a moisture content of 9 mg/kg. 400 ml oil and the paper (7.5 g) or paper-wrapped copper strip (paper: 7.5 g) were placed in the same
glass vial (500 ml), respectively, as presented in Figure 1. For each sample of NK, NKC, PK and PKC, there are 8 vials. The space above the oil was filled with nitrogen and the vial was sealed tightly. After that, all vials were placed in a temperature controlled bath at 130°C with a temperature deviation of 0.1°C for accelerated thermal ageing. Figure 2 shows the photographs of the sample prepared well. The parameters of oil and paper were analyzed after ageing different times.

![Figure 2. Photographs of initial ageing samples](image)

### 3. Results and Discussions

#### 3.1. Oil acidity

As a direct parameter to reflect the ageing degree of insulation oil, the oil acidity of NK, NKC, PK and PKC samples are shown in Figure 3. The oil acidity was measured according to ASTM D974-04. The acidity values presented in this paper is the average of three testing values for each sample at room temperature 27±0.2 °C. The accuracy of the measurement is about ±0.005 mg KOH/g. Oxidation of oils can be accelerated by acids and catalysed by copper substance, such as copper ion and heavy copper-organic compounds [12, 13]. It can be seen from Figure 3 that NKC samples with copper have higher oil acidity than NK samples without copper all the time. However, PKC samples with copper have lower oil acidity than PK samples without copper before ageing 29 days, after which the oil acidity of PKC samples become higher than PK samples. Besides, the oil acidity of NK and NKC is lower than oil acidity of PK and PKC after ageing the same time at 130 ºC, respectively. It can be seen from Figure 3 that Copper play a catalyse role on the whole ageing of naphthenic oil, while the catalyse role becomes obvious in paraffinic oil after ageing 29 days.

![Figure 3. Changes of oil acidity during oil-paper insulation samples ageing process](image)

#### 3.2. AC breakdown voltage of oil

The most important and therefore most often checked parameter of a liquid insulation is the breakdown voltage. The AC breakdown voltage of oils in NK, NKC, PK and PKC samples as function of the ageing time is shown in Figure 4. The AC breakdown voltage of oil was measured according to IEC 60156. The AC breakdown voltage value presented in this paper is the average of six testing values for each sample at room temperature 27±0.2 °C. The accuracy of the measurement is 1.5%. The AC breakdown voltage of oil in NK sample is higher than oil in NKC sample during whole ageing.

![Figure 4. Breakdown voltage of insulation oils versus ageing time](image)
process, except for the sample aged 11 days. The AC breakdown voltage of oil in PK sample is also higher than oil in PKC sample during all the ageing process. It indicates that copper substance existence in oil-paper insulation during the ageing process weaken the oil dielectric property. In addition, regardless of oil-paper insulation sample with copper or without copper, Figure 4 shows that the AC breakdown voltage of naphthenic oil is nearly all higher than that of paraffinic oil during the thermal ageing process. This presents that the naphthenic oil performs a better dielectric characteristic than paraffinic oil at the same ageing condition.

3.3. The content of copper substance dissolved in oil
Copper substance such as copper ion and heavy copper-organic compounds play an important role in the ageing process of oil-paper insulation, which is shown above. The oil acidity of paraffinic oil is much higher than naphthenic oil during the whole ageing process (Figure 3). The increased oil acidity will increase the corrosion rate of copper. Therefore, the copper corrosion in PKC sample is more serious than that in NKC sample, as presented in Figure 5. Figure 5 shows that the content of copper substance dissolved in paraffinic oil is larger than that in naphthenic oil before ageing 35 days. However, when sampled at 35 days, the sludge was observed in all aged samples, which is more obvious in PK and PKC sample. The copper-organic compounds in the oil will sediment together with the sludge and hence decrease the copper content dissolved in oil [12, 14, 15]. The more formation of insoluble sludge will cause more heavy copper-organic compounds sediment in the sludge. Consequently, a decreased of the content of copper substance dissolved in oil is observed after ageing 35 days, and the content of copper substance dissolved in paraffinic oil is less than that in naphthenic oil.

3.4. Moisture content of paper
The absolute moisture content of oil impregnated paper of NK, NKC, PK and PKC sample is shown in Figure 6. Moisture moves between the paper and insulation oil to reach equilibrium in terms of relative saturation. Therefore, the moisture content of oil impregnated paper of NK, NKC, PK and PKC sample is undulate. It can be seen from Figure 6 that the copper has great effect on the moisture content of oil impregnated paper in the ageing process. The PK and PKC sample nearly has higher moisture content than the NK and NKC sample in the whole ageing process. It’s noteworthy that the moisture content of paper aged in PKC is higher than that aged in PK, and the moisture content of paper aged in NKC is higher than that aged in NK.

Figure 5. Content of copper substance dissolved in oil

Figure 6. Moisture content in paper varying with ageing time
3.5. Paper property

The difference in appearance between the innermost papers near to the copper plate aged in NK, NKC, PK and PKC sample are shown in Figure 7. The aged paper becomes more brittle with ageing time increased, especially for the paper aged in PK and PKC sample. Visually, the longer time of the paper aged, the more discoloration of the paper became. After ageing 77 days, the paper in paraffinic oil was almost black, while that in naphthenic oil was yellow. These observations appear to predict a faster degradation rate of paper in paraffinic oil than in naphthenic oil.

Compared with the paper aged in NK and PK, it should be emphasized that that there is obvious product deposition phenomenon in NKC and PKC sample when sampling at 77 days. Copper deposition in the insulating paper has been widely reported in recent years [3-11] and it is copper dissolution by corrosion that subsequently leads to copper deposition on insulating paper. From a chemical perspective, copper can, in principle, be deposited in the form of oxides, sulphides, or other compounds and complexes, or even as metallic copper after redox reactions [12]. The innermost paper near to the copper plate of NKC samples aged for 77 days were measured by SEM. Before the SEM measurement performed on the paper sample, the paper was gold coated. Figure 8 shows that there is copper element deposited on the surface of paper.

![Figure 7. Colour of the innermost paper near to the copper plate in NK, NKC, PK and PKC sample](image)

(a) The innermost paper near to the copper plate in NK aged for 77 days

(b) The innermost paper near to the copper plate in NKC aged for 77 days

![Figure 8. SEM/EDS result of innermost paper near to the copper plate in NK and NKC aged for 77 days](image)
4. Conclusions

In this work, thermal ageing test of four combinations of oil-paper insulation samples including naphthenic oil + Kraft paper (NK), naphthenic oil + Kraft paper + copper (NKC), paraffinic oil + Kraft paper (PK) and paraffinic oil + Kraft paper + copper (PKC) at 130 °C has been carried out, where observations on naphthenic oil-paper insulation and paraffinic oil-paper insulation samples both with and without copper were compared, respectively. The following conclusions are able to be drawn:

NKC samples with copper have higher oil acidity than NK samples without copper all the time. However, PKC samples with copper have lower oil acidity than PK samples without copper before ageing 29 days, after then the oil acidity of PKC samples become higher than PK samples. Copper play a catalyse role on the whole ageing of naphthenic oil, while the catalyse role becomes obvious in paraffinic oil after ageing 29 days.

Copper substance existence in oil-paper insulation during the ageing process weakens the oil AC breakdown. Naphthenic oil performs a better AC breakdown characteristic than paraffinic oil at the same ageing condition.

The content of copper substance dissolved in paraffinic oil is larger than that in naphthenic oil before ageing 35 days, while after then, a decreased of the content of copper substance dissolved in oil is observed, and the content of copper substance dissolved in paraffinic oil is less than that in naphthenic oil.

Copper has great effect on the moisture content of oil impregnated paper in the ageing process. SEM results show that there is copper product deposited on the insulating paper surface.

5. References

1. Linhjell D, Lundgaard L E, Gafvert U 2007 IEEE Transactions on Dielectrics and Electrical Insulation 14 156
2. Wood-Mallock J C, Wood L G 1958 J. Inst. Pet. 44 320
3. CIGRE WG A2-32. 2007 Copper sulphide in transformer insulation. ELECTRA, No. 230.; 12
4. CIGRE TF A2.31. 2006 Copper sulphide in transformer insulation. ELECTRA, No. 224, 20
5. CIGRE WG A2-32. Copper sulphide in transformer insulation. Interim Report No.1, 2006.
6. Bengtsson C, Dahlund M, Hajek J. et al. CIGRE, Paris, 2006.
7. ABINEE, Workshop on Corrosive Sulphur in Oil, June 2-3 2005, Sao Paulo, Brazil. Available: http://www.cigre-a2.org/Site/Publications.
8. Kobayashi T, Tanimura J, Murakami H, et al. 2007 CIGRE, SC A2 & D1, Colloquium, Belgium.
9. Eechhoudt S, Van J, Peteghem, Kinable L 2007 CIGRE, SC A2 & D1, Colloquium, Belgium, PS2-05.
10. Bastos G M. 2007 CIGRE, SC A2 & D1, Colloquium, Belgium, P80-01.
11. Scatiggio F, Tumilatti V, Maina R, et al. 2008 IEEE Trans. Power Delivery 23 508
12. Wiklund P, Levin M, Pahlavanpour B 2007 IEEE Electrical Insulation Magazine 22 6
13. Liao R J, Tang C, Yang L J, et al. IET Electr. Power Appl. 2009 3 407
14. Thomson C N1958 J. Inst. Petrol. 44 295
15. Kalantar A, Levin M 2008 Lubrication Science 20 223

Acknowledgements

All the authors thank the Scientific Research Foundation of SKL of Power Transmission and System Security (2007DA10512708103) for the financial support provided.