Corrosion Science 84 (2014) 172–179

Contents lists available at ScienceDirect

Corrosion Science

journal homepage: www.elsevier.com/locate/corsci

Contact-based corrosion mechanism leading to copper sulphide deposition on insulating paper used in oil-immersed electrical power equipment

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ARTICLE INFO

Article history:
Received 6 December 2013
Accepted 16 March 2014
Available online 24 March 2014

Keywords:
A. Copper
B. SEM
B. XPS
C. Interfaces
C. Sulphidation

ABSTRACT

XPS and EDX were used to study Cu_xS deposition in Kraft insulating paper obtained from ageing paper samples in contact with a copper sheet, in mineral oil containing dibenzyl disulphide (DBDS). Qualitative and quantitative evidence of Cu_xS were obtained from bulk and surface analyses of insulating paper provided by the different depth resolution of the techniques used. The influence of [DBDS], oxygen, time, and Cu-paper contact upon the formation and mobilisation of Cu_xS were studied. A contact-based mechanism to explain Cu_xS contamination on paper and its displacement was proposed. The role of O_2 in enhancing Cu_xS displacement was also investigated.

1. Introduction

Copper has been a preferred material for conductors since the very beginning of electricity distribution due to its high conductivity, second only to silver, combined with moderate cost and favourable physical properties. Reliant on copper for the majority of its conductive equipment, the electrical power distribution industry is not new to corrosion issues and transformers, which are an integral part of modern ac power networks, are vulnerable to corrosion-related failure. The transformer is essentially a static electrical machine that steps up or down the voltage level in order to reduce losses at transmission level, while reducing insulation requirements at distribution level. Transformers consist of three main components: winding conductors, a dielectric system and magnetic core [1]. The insulation materials, commonly referred to as the dielectric system, are known to be the weakest point of the transformer and among them paper is the most critical [2]. Hence insulating materials define the lifespan of these systems. The most widely used insulation fluid is mineral oil and the most common material wrapped around copper conductors is Kraft paper. The oil serves the dual purpose of providing insulation and cooling to the transformer, while paper provides the main electrical insulation between the turns of the conductor in a coil [1].

Corrosion of copper is still studied extensively as the major technological issue in its use, as metal or alloy, in specialist and everyday applications. Its behaviour in corrosive environments is strongly dependent on the media in which it is immersed. Recent studies on applied copper corrosion in different media such as seawater [3], oil [4,5] and fuels [6] reflect the current relevance of the problem.

It is known that copper is prone to react with active sulphur species [7,8] present in oil, such as dibenzyl disulphide (DBDS) [9] leading to the formation of copper sulphides inside the transformer [10,11]. Although the presence of sulphur in all refinery products has been drastically reduced during the last twenty years, due to advances in the petrochemical industry, the occurrence of corrosive oils has been increasing [12]. The formation of conductive materials inside transformers can lead to the disruption of the insulation and therefore failure, often catastrophic, of the machine [13]. The routine replacement of the oil within the transformer does not generally provide a practical solution due to its high cost and environmental impact, therefore mitigation strategies such as passivation or reclamation were suggested by CIGRE (International Council on Large Electric Systems) [14]. In the last

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http://dx.doi.org/10.1016/j.corsci.2014.03.024
0010-938X/

decade several studies have been carried out to understand the mechanism [14–19] and the impact of environmental factors and remedial procedures on corrosion in paper-oil based transformers.

Studies on the influence of oxygen [18], temperature, type of oil, concentration of corrosive sulphur compounds [20], diffusion of copper sulphide through paper layers [21] and passivators [22] were performed and the outcomes have been translated into standardised procedures used worldwide such as EN62535 [23].

DBDS is widely considered to be the corrosive compound which is the major cause of Cu_xS deposition on paper insulators in transformers [14]. Consequently, DBDS has been widely employed as the chemical to simulate a corrosive environment in a non-corrosive (ASTM D7671) oil matrix.

One main reaction mechanism for Cu_xS deposition has been proposed in the literature to explain observations on in-service or failed units and it can be defined as a two-step oil-based process [17]. It is proposed that DBDS-like compounds are able to form complexes with copper, which diffuse through the oil. These copper and sulphur-containing species can be absorbed by the paper insulation where they then decompose giving rise to copper sulphide, dibenzyl sulphide (DBS) and bibenzyl (BiBZ) (Fig. 1) [17].

Depositions can eventually lead to either a thermal insulation failure or electrical breakdown between two adjacent conductors [12]. Although an oil-based mechanism can account for empirical observations such as the presence of deposits on outer paper layers far from the copper surface, it does not explain the bulk of copper sulphide deposits that degrade the Kraft paper dielectric properties to a point that causes the transformer to fail. Currently, the only standard method available to determine the degree of deposition of Cu_xS on paper is qualitative. The EN 62535 IEC standard corrosion test gives a verbal description of how Cu_xS deposits on paper may appear visually (e.g. metallic appearance from shiny to almost lustreless), which sometimes is insufficient when trying to produce Kraft paper samples with a constant and homogenous distribution of Cu_xS. The ASTM D1275-06 refers to the ASTM D130 Test Method, which provides the user with a colour chart to better analyse the degree of corrosion of a copper sample (Fig. 2).

Here, we describe visual and spectroscopic (EDX and XPS) studies of insulating paper samples aged in mineral oil containing DBDS. It is proposed that the formation and migration of complexes is not the only mechanism taking place in oil insulated apparatus for the formation of Cu_xS [17], and evidence is presented to support the contribution of a contact-based mechanism in the overall process of Cu_xS deposition on insulating paper in transformers. As a result, a new bifurcated mechanism is proposed to explain both surface and bulk contamination of insulating paper in transformers. To enable these investigations, the optimization of a laboratory procedure to obtain contaminated paper samples, of sufficient size to be used in multiple analyses including electrical and spectroscopic studies, is also described.

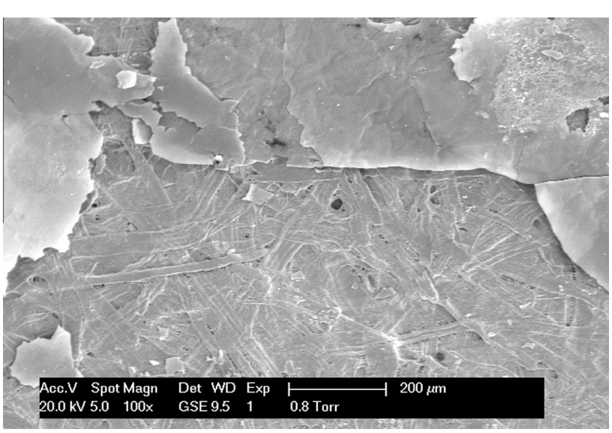

Fig. 1. ESEM picture of a paper sample showing extensive copper sulphide contamination after 7 days ageing with copper under an air atmosphere with 10,000 ppm of DBDS.

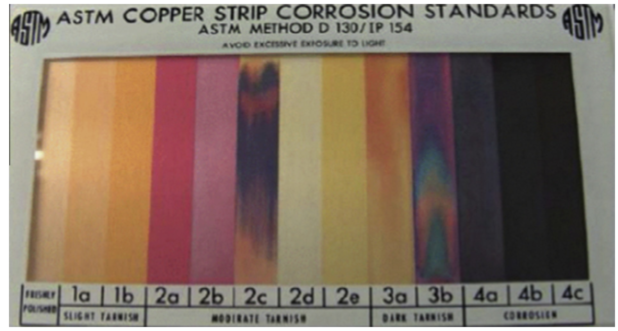

Fig. 2. ASTM D130 colour chart for copper corrosion evaluation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2. Materials and methods

2.1. Production of paper samples

DBDS (Sigma Aldrich, 98%) was used in the sample preparation. The mineral oil used was Nytro Gemini X (Nynas). Gemini X is an inhibited insulating oil, with maximum total sulphur content of 0.05%, no detectable DBDS, no metal passivator additives and non-corrosive according to the standard corrosion test EIC 62535 [23]. The copper square sheet used was a grade C106 with a thickness of 0.5 mm and an area of 1800 mm^2. The paper used was standard electrical insulation Kraft paper with a thickness of 0.07 μm. Plastic zip ties where used to keep contact pressure between paper and copper. Ageing experiments were performed in a crystallising dish (140 mm outer diameter by 73 mm high). DBDS (906 mg) was dissolved in warm (oil temperature between 50 °C and 70 °C) Gemini X mineral oil (453 g, 512 mL) with efficient mechanical stirring using a stirrer-hotplate to ensure thorough mixing of the oil, to obtain a clear solution (final DBDS concentration 2000 ppm). Square copper plates were curved to a roughly constant radius, giving rise to concave and convex surfaces. The convex surface of the curved copper plate is therefore in close contact with the inner side of insulating paper (Fig. 3).

Immediately prior to the experiment, the copper plates were polished and washed with cyclohexane to remove surface impurities. Kraft paper was handled with gloves and stored in a dry and oxygen free environment. Prior to the experiment the paper was cut to a dimension of 90 mm by 180 mm, wrapped around the conductor and secured using plastic zip ties to increase surface contact. The covered copper plates were then placed in the oil. Depending on the type of atmosphere, nitrogen or air, a vacuum or fan oven was used respectively. For experiments conducted

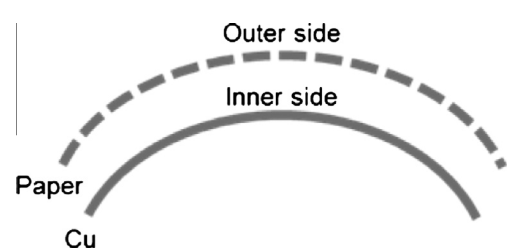

Fig. 3. Schematic representation of the sample subject to ageing.