Investigating the Physiochemical Effects of Verdigris Contamination found on a Polymeric Cable Sealing End

S. Thakur*, T. Andritsch, P. L. Lewin
Tony Davis High Voltage Laboratory
University of Southampton
Southampton, UK
*s.thakur@soton.ac.uk

A. V. Shaw
Department of Chemistry
University of Southampton
Southampton, UK

O. Cwikowski
Engineering and Asset management
National Grid Electricity Transmission
Warwick, UK

***Abstract*- A Cable sealing end is a crucial power system component as it is responsible for the vital task of successfully terminating cables. Recent reports on the diagnosis of ex-service units have led us to investigate possible contaminations that could impact the dielectric properties of a cable sealing end. Verdigris, often blue/green in color, is one such contaminant that is observed on the surface of a cable stalk. This investigation aims to understand the possible cause of this contamination and its impact on the dielectric liquid used inside a polymeric cable sealing end. To achieve this, the current study is devised in two parts. First, a sample of the verdigris is scraped off from the cable stalk surface and analyzed. The elemental composition of the blue verdigris is analyzed using energy-dispersive X-ray methods on a scanning electron microscope. Second, sonication ageing tests are performed on samples of silicone oil that have been contaminated with verdigris. Elemental analysis shows traces of carbon, oxygen, sodium, silicon, tin and copper contaminations as the primary components of the verdigris present in different percentage. The results from the second half of the study obtained shows an increment in dielectric permittivity and moisture measurements, whereas not much change was reflected in the UV-vis analysis when compared with fresh oil sample.**

I. INTRODUCTION

Risk of contamination is a fear that can directly impact one's lifetime. Electrical equipment is often exposed to high stress which may be a cause or consequence of high contamination risks. The recent reports of ex-service cable sealing end (CSE) units mention the presence of blue verdigris on the connector stalk beneath the seal area. This is suspected as a possible by-product of moisture ingress in the CSE. Another point of interest in the report is the level of acetylene present in 21 out of 28 aged CSE, 5 of which were found to have blue verdigris

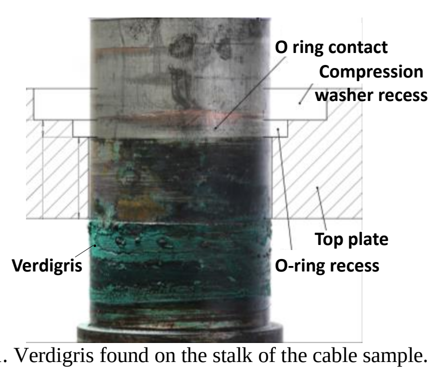

Fig.1. Verdigris found on the stalk of the cable sample. Note: The verdigris was only found below the seal and not above the seal.

below the "O" ring seal [1]. It is suspected that ingress of moisture leading to its reaction with copper and the insulating materials in contact could be responsible for the formation of contamination on the cable stalk.

Zhang et al., [2] have reported that the fundamental cause of the breakdown of porcelain oil-filled CSE was the flocculation produced by aged silicone oil filled in the CSE. The breakdown of cable insulation was due to the combined action of high electric field and moisture near the stress cone. High moisture saturation in the silicone oil causes the water branch discharge on the surface of the cable insulation when exposed to electric stress and is located in the region of flocculation above the stress cone. Singh et al., [3] have reported the presence of carbonization on the cable near the interface of the semiconducting component of the stress cone and the cable. The possible cause discussed in the report is "poor preparation" of the CSE, especially in the critical transition area.

These reports raise concerns about possible presence and effects of verdigris contamination leading to a need for an extended study to understand the nature and impact of the contamination. Since the blue verdigris is likely to come into contact with the silicone oil (liquid dielectric used in polymeric CSE), it can be identified as a possible contaminant to the oil. As such, how it affects the ageing of the oil was found to be worth investigating. Based on this understanding, the current study is devised in two parts, in the first section a sample of the verdigris is scraped off from the cable stalk surface and analyzed. In the second half, some more of the scraped off verdigris is added to silicone oil sample and sonicated for a prolonged time. In our previous work, sonication treatment of the silicone oil has shown theoretical resemblance to electrical stress when used to age the oil [4].

II. SAMPLES AND TESTING

A. Samples and sonication treatment

The elemental composition of the blue verdigris was analyzed using energy-dispersive X-ray (EDX) methods on a scanning electron microscope (SEM). The blue verdigris (Fig.1) was scraped off and attached to a stub with black conducting tape.

To induce the effect of external stress on the chemical structure of silicone oil and understand the effect of verdigris contamination, silicone oil (Xiameter PMX 561) was kept in a sonication bath with and without the verdigris contamination. The bath used for this treatment was a Sonocool 225 supplied by Bandelin, operating at 100 % power, 40 °C for 420 hours. The treated oils (with and without blue verdigris contamination) were then analyzed and compared with the original unaltered oil referred as virgin oil sample. The samples retrieved after sonication treatment are referred to as sonicated silicone oil and sonicated silicone oil + blue verdigris in the analysis.

B. EDX Analysis of Blue Verdigris

The maps are generated by linking a standard scan such as an SEM to the EDX software so that it knows its exact position. The elemental mapping tool was used in several different areas of the stub to analyze several areas of verdigris. For every position of the scan, the x-rays generated by the interaction of the SEM beam and the sample are collected. The software uses a database to decide the element to which that energy of x-ray belongs.

For each element detected (or user-selected) a greyscale heat map is generated, where the brightness of each position on the image corresponds to more x-rays attributed to that element have been detected. If the raw data of the scan is analyzed each location on the scan is assigned a number. That number indicates the number of counts of x-rays detected at that location. This data can only be used comparatively (using the relative ratio) and not quantifiably because the number of counts may indicate the presence of the element and give a good indication of how the element varies across a sample but not more. The comparative brightness of the images on the document does not relate to the quantified measurements.

C. UV-vis Analysis

The UV- visible spectrometry of different oil samples were recorded using a Perkin Elmer Lambda 35 spectrometer. 10 mL PMMA cuvettes were used for the examination (path length 10 mm) and the wavelength range of 200 to 700 nm was selected for performing the scans.

D. Dielectric Response Analysis

The dielectric response of the oil samples was analyzed through dielectric dissipation factor (DDF) and permittivity tests at room temperature (20 ºC). A liquid test cell supplied by Solartron Analytical (model 12964A), operating at 200V was used along with an Omicron Spectano 100. The permittivity of air with a specified electrode distance (0.5 mm) was used as a reference (to obtain ε' values of 1) and then the respective oil was poured into the fixed electrode gap and measured. The frequency range of measurement was varied from 10^{-1} Hz to 5 kHz in FDS (Frequency Domain Spectroscopy) mode.

III. Results

A. EDX Analysis of Blue Verdigris

The results are presented in Table I and a representative selection of the maps are shown in Fig. 2. The images are zoomed 1500 times.

Notes for interpreting these results:

- If the standard deviations are > 1/3 of the weight % then there is no significant presence of that element.
- Sodium, and to a lesser extent potassium, are common contaminants so there is no immediate concern about the presence of these, particularly at the low weight % observed. This equipment has around a 0.1 wt.% sensitivity depending on the element.

TABLE I

Summary of the EDX Data Investigating the Identity of the Blue Verdigris

Element	Area 1 Weight % ± standard deviation	Area 2 Weight % ± standard deviation	Area 3 Weight % ± standard deviation	Area 4 Weight % ± standard deviation
Carbon	12.69 ± 0.39	8.67 ± 1.00	13.89 ± 1.09	11.61 ± 0.99
Oxygen	61.64 ± 0.4	37.16 ± 0.39	32.55 ± 0.38	23.55 ± 0.33
Sodium	14.03 ± 0.22	1.29 ± 0.17	0.84 ± 0.16	0.66 ± 0.13
Silicon	0.76 ± 0.05	2.25 ± 0.07	3.92 ± 0.07	2.86 ± 0.06
Potassium	--	0.95 ± 0.07	0.57 ± 0.05	0.43 ± 0.04
Copper	7.62 ± 0.18	29.24 ± 0.32	23.66 ± 0.29	21.66 ± 0.27
Tin	--	3.28 ± 0.17	1.12 ± 0.13	0.85 ± 0.11

The mapping shows that the aluminium content is low compared to copper. These results show that copper, oxygen and carbon make up the majority of the verdigris. We suggest that this comes from the CSE core and silicone rubber parts. These elements were spread uniformly across the sample areas studied. The results showing a high copper content was not surprising given the color of the verdigris. We suggest that the copper is present in the form of copper oxide, consistent with the copper core being exposed to the air or water ingress.

The mapping shows that the silicon, tin and aluminium were present in localized regions, suggesting the presence of 'chunks'. This is consistent with the locations where the blue verdigris was collected. However, there was no significant presence of lead, which is somewhat surprising given that lead would normally be a part of the CSE.

The sum of the weight % does not equal 100% indicating the error in the measurement, however, it is a common observation. Normally, ±3% from 100% is considered good accuracy for this technique on an ideal sample. The variation in total percentages may be down to the sample topography.

Overall, we believe these results to be unsurprising – the components of this verdigris are all originating from the CSE and are localized in the region on the copper core likely due to either water ingress/environmental exposure or the structure of the CSE meaning that verdigris collects at this point. Also, we do not have large amounts of external particles sneaking past the O-ring, confirming that even though the O-ring might look like a weak link, there appears nothing contaminants in the analysis that wouldn't be part of components of the CSE anyway, or at least not in significant amounts.

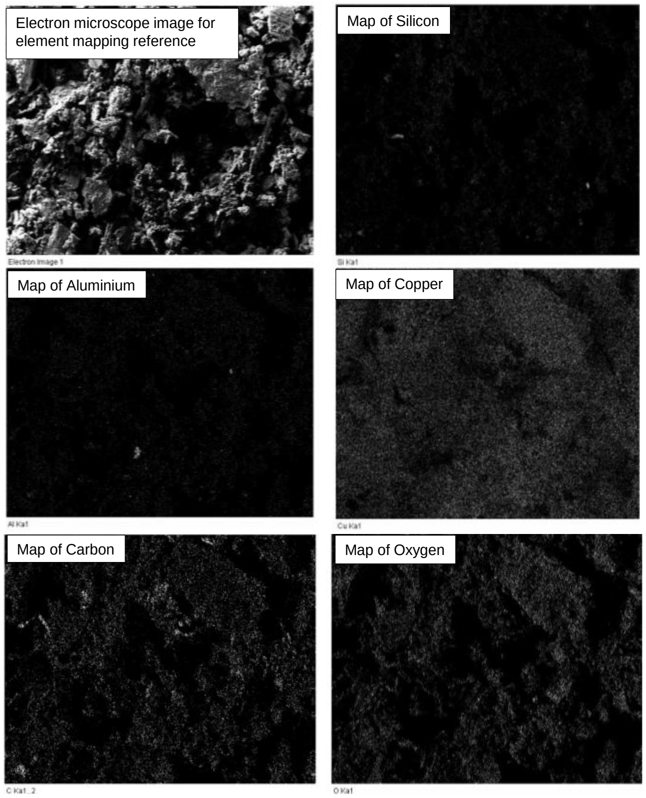

Fig.2. EDX mapping results of one out of four areas analysed, (zoomed 1:1500) (Table I).

B. Physical changes in sonicated silicone oil in the presence of blue verdigris

Fig. 3 shows the image of silicone oil and blue verdigris before and after sonication (the white smudges are on the outside surface of the glass). The results of the sonicated oil in presence of verdigris obtained are summarized here in contrast with plain sonicated silicone oil sample and the virgin silicone oil (Table II).

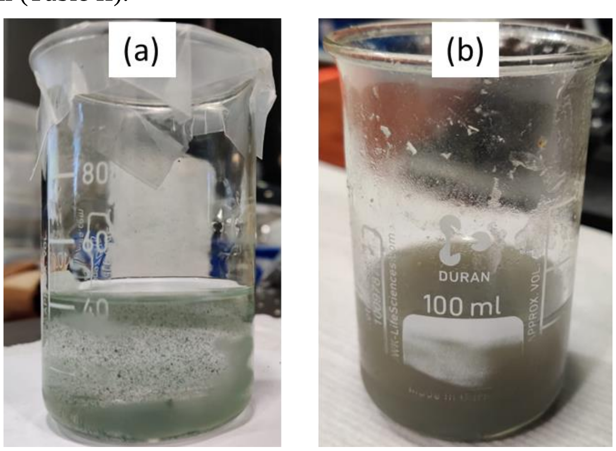

Fig. 3. Image of silicone oil + Blue Verdigris before and after sonication.

TABLE II
Summary of the data obtained on sonicating silicone oil with blue verdigris in comparison with virgin oil and sonicated oil sample.

Property	Virgin Silicone Oil	Sonicated Silicone Oil	Silicone Oil Sonicated in Presence of Blue Verdigris
General Observation	Colorless and odorless, Poured smoothly and easily	Transparent Partial gel-like appearance, Exhibited higher viscosity	Opaque (dark grey) Partial gel-like appearance, Poured like lumps of gel mixed in liquid
Moisture content (ppm)	76.8	97.4	417.1
Dielectric spectroscopy	The real part of the dielectric permittivity (ε')-frequency independent (value close to 2.75) A low dielectric loss at low frequency	An increase in real and imaginary permittivity is recorded	Increase in ε' (around 2.84), imaginary permittivity and losses are not affected by sonication
UV-vis analysis	No differences detected		

The moisture content is observed to increase during sonication process. This is similar to the effects of sonication found in earlier studies [4]. Silicone oils extracted from ex-service CSE have shown a similar increase in moisture indicating blue verdigris as potential detrimental contamination [5].

C. UV-vis analysis

There is a change in appearance as seen in Fig. 3, to understand change UV-vis spectroscopy was conducted for the three samples. The results of UV-vis spectroscopy analysis on the oil samples are shown in Fig. 4.

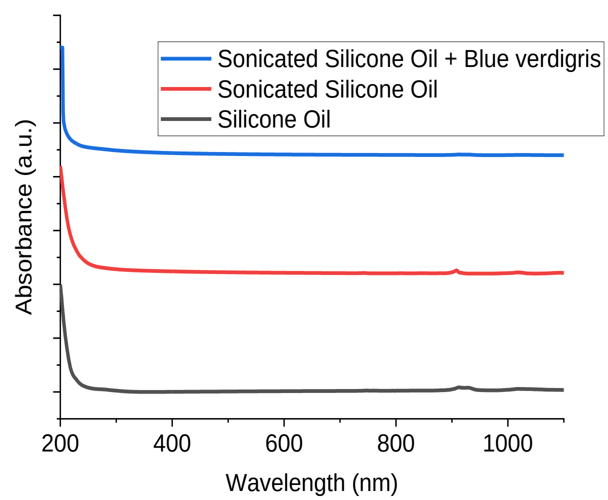

Fig. 4. UV-vis analysis of silicone oil, sonicated silicone oil (without any contaminant) and silicone oil sonicated with blue verdigris.

Oil sonicated with blue verdigris shows that sonication does not lead to any detectable changes in the UV-vis spectroscopy.

D. Dielectric response analysis

The dielectric parameters of the four oils under investigation are shown in Fig. 5.

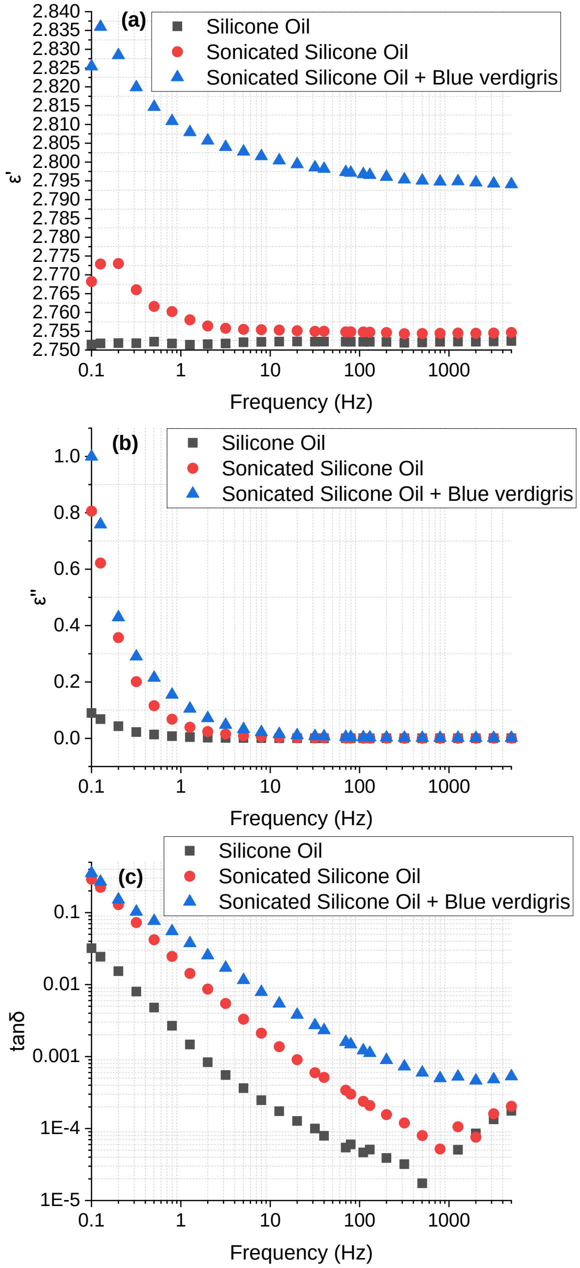

Fig. 5. Dielectric spectra silicone oil, sonicated silicone oil and silicone oil sonicated with blue verdigris, (a) real part, (b) imaginary part and (c) tanδ of the relative complex permittivity. Measurements are taken at ambient temperature.

For the silicone oil sonicated with blue verdigris, there is an increase in the magnitude of real permittivity with a slight decrease at lower frequencies. This is simlar to the behavior observed in ex-service oil and could be explained as a consequence of small impurities in the oil [6]. However the values area affected in the second decimal digit and thus can be viewed as insignificant. This could be related to the increase in moisture content which often leads to increased permittivity at low-frequency range. However, the dielectric dissipation losses (tan(δ)) is found to be unaffected by the sonication treatment and the presence of verdigris.

IV. Conclusions

The chemical analysis of the verdigris suggests that it is majorly composed of copper present in the form of copper oxide, consistent with the copper core being exposed to the air or water ingress. The oil contaminated with the verdigris does not exhibits much difference in the chemical composition of oil post sonication. However, an increase in moisture content and dielectric permittivity was observed. Whether this increased moisture would create a humid environment inside the CSE which could lead to the growth of the verdigris and not vice versa is another possibility reflected by the ageing results. These results could form a base for understanding the effect of verdigris contamination on the dielectric insulation strength of cable accessories which could be a crucial analysis to develop health indicators for more efficient condition monitoring.

Acknowledgement

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