IEEE Access
Multidisciplinary : Rapid Review : Open Access Journal

Received December 2, 2021, accepted January 10, 2022, date of publication January 13, 2022, date of current version January 27, 2022.

Digital Object Identifier 10.1109/ACCESS.2022.3142960

Impact of DBDS and Silver Sulfide on the Performance of Thermally Aged Mineral oil Impregnated Pressboard Material

S. K. AMIZHTAN[1], A. J. AMALANATHAN[1], R. SARATHI[1], (Senior Member, IEEE), AND R. VINU[2]

[1]Department of Electrical Engineering, Indian Institute of Technology Madras, Chennai 600036, India
[2]Department of Chemical Engineering, Indian Institute of Technology Madras, Chennai 600036, India

Corresponding author: R. Sarathi (rsarathi@iitm.ac.in)

This work was supported by the Science and Engineering Research Board (SERB), New Delhi, India, under Grant CRG/2020/003525/EEC, on advanced transformer insulation.

ABSTRACT The corrosive sulfur compounds present in the mineral oil causes the formation of dibenzyl disulfide (DBDS) complex and it can also erode the on-load tap changing selector contacts leading to generation of silver sulfide (AgS_2).The present work reports the effect of DBDS and Ag_2S concentrations in mineral oil on thermally aged pressboard material. The results demonstrate that surface discharge inception voltage (SDIV) is higher for the aged pressboard specimen. The higher concentrations of DBDS showed a reduction of more than 50% in the magnitude of SDIV compared to its effect with the addition of Ag_2S. The surface potential analysis indicates a higher initial potential for the aged specimens with an increased half lifetime. In addition, only deep traps observed on the aged specimens with a slight right shift in its trap energy level. The mechanical strength of aged pressboard specimens with DBDS and Ag_2S is understood using tensile testing and simultaneous analysis is captured using Digital Image Correlation (DIC) technique to understand its strain percentage at different areas on the pressboard material during its elongation. The laser induced breakdown spectroscopy (LIBS) analysis is performed to identify the elements responsible for thermal ageing such as carbon, copper and sulfur on the surface of pressboard material. The plasma temperature calculated from sulfur peaks is higher for DBDS aged specimen compared to AgS_2 and a linear correlation is observed on the LIBS intensity with ageing duration. Further, the Principal Component Analysis (PCA) is used for its classification on the degradation of pressboard due to the diffusion of both copper and silver sulfide from the mineral oil. The two principal components (PC1 and PC2) provided a higher variance of 99.8% with a clear classification observed between the unaged and aged pressboard specimens due to the addition of both DBDS and Ag_2S in mineral oil.

INDEX TERMS Thermal ageing, sulfur, surface discharge, fluorescence, trap density, DIC, strain, elongation, LIBS, plasma temperature, PCA.

I. INTRODUCTION

The power system components, such as transformers and cables, employ liquid dielectrics as an insulating medium and coolant, and as an arc quencher in high voltage circuit breakers [1]. They serve as the bulk insulation medium in transformers, with cellulose paper/pressboard material serving as the winding conductor insulation. Since the early usage of AC systems for transmission and distribution of electrical power, researchers have focused on the dielectric and physico-chemical characteristics of both liquid and solid insulants. For more than a century, there have been various research focused on the usage of mineral oils and other hydrocarbon-based liquids for transformer insulation and cooling. These fluids have better dielectric characteristics with its easy extraction from the crude oil compared to other fluids which results in the discharge of toxic pollutants into the atmosphere [2]. Thus, considering the lower cost of production, mineral oil filled transformers are still widely used in the industry nowadays. During the operation of power transformers, the liquid as well as solid insulants are subjected to multiple stresses (electrical, thermal and chemical) leading to the formation of degradation

The associate editor coordinating the review of this manuscript and approving it for publication was Jinhua Sheng.

products such as organic acids and sludges, which reduces the lifetime of transformers [3], [4].

The corrosive sulfur compounds present in the mineral oil has been the major reason for the formation of copper sulfide (Cu_2S) in the insulating paper/pressboard [5]. Amimoto *et al.* [6] have shown that Cu_2S is formed via the interaction of dibenzyl- disulphide (DBDS) present in oil with copper to produce the DBDS-Cu complex, which is then decomposed into Cu_2S, dibenzyl sulphide (DBS), and bibenzyl (BiBZ). Silver coating is normally used for on-load tap changing (OLTC) selector contacts for its superior electrical, mechanical, and thermal characteristics [7]. The corrosive sulfur compounds from the mineral oil can react with the silver coating on the tap selector components to create a silver sulfide layer on the surface, which corrodes the contacts and forms a resistive coating [8]. The silver sulfide layer, being conductive in nature, can detach from the tap selector contacts and diffuse into the insulating oil degrading its dielectric properties. Although there have been various reports on the mechanism of copper sulfide formation towards its impact on the dielectric properties of both insulating oil and pressboard [9], [10], the diffusion of silver sulfide towards the pressboard material and its associated physico-chemical interactions are not well understood in the existing literature. Therefore, in the present work, the impact of ageing of DBDS and Ag_2S containing mineral oil on the insulating pressboard material has been studied in detail using a wide array of analytical instrumentation techniques.

Jusner *et al.* conducted a thorough investigation of the effects of thermal stress on the cellulose insulation impregnated in mineral oil, and inferred the formation of low molecular weight organic molecules and acidic residues caused by the breakage of covalent bonds present in the oil and cellulosic pressboard material [11]. These intermediate compounds can further hasten the decomposition of pressboard increasing the surface charge accumulation [12]. The charge carriers on the solid insulation can alter the localised electric field and if the tangential electric field is greater than 1-2 kV/mm [13], it can initiate the surface discharge phenomenon which is one of the major reasons for the failure of the transformer insulation. The UHF method has been generally utilized to identify such incipient discharges, and its defect by evaluating the signal characteristics. Recently, optical fibers [15] are gaining importance for detecting corona discharges. In the present work, fluorescent fiber technique has been adopted for the identification of surface discharges. Upon thermal ageing, the mechanical strength of the pressboard insulation decreases with reduction in its degree of polymerization [16]. Moreover, the tensile strength of the solid insulation inside the transformer has been related directly to its deterioration rate [17]. Therefore, a realistic assessment of the degree of degradation is made by measuring the tensile strength of the pressboard specimens.

The laser induced breakdown spectroscopy (LIBS) is used for the quantification of elements present in the materials and is now widely used in various applications [18]. However, in the case of transformers, the application of LIBS in a real-time context is still in its early stages. Moreover, it is not only important to understand the elemental characterization of thermally aged pressboard material with the identification of sulfide ions, but it is also necessary to provide a suitable condition monitoring technique to track the health index of the transformer insulation. In this regard, principal component analysis (PCA) enables the categorization based on the degree of degradation involved during the ageing.

The present work considers the effect of DBDS and Ag_2S diffusion towards the pressboard material through various surface characterization analysis with novel digital image correlation (DIC) technique adopted for its tensile strength and multivariate analysis of LIBS spectra coupled with PCA for its classification on the aged pressboard specimens.

II. EXPERIMENTAL DETAILS

A. THERMAL AGEING

The preparation of insulation test samples was done by immersing in high-density insulation pressboard (1.2 g/cm^3) procured from a transformer manufacturer (Andrew Yule Pvt. Ltd). The sample thickness was 1.5 mm. A 4×4 cm pressboard sample used in this investigation was dried for 24 hours at 105°C before being immersed in oil (IEC 60641-2) for thermal ageing studies [19]. The dry pressboard specimen was then wrapped with a thin copper sheet (thickness 0.5 mm), and impregnated for another 24 hours at 90°C in a beaker containing mineral oil. The copper sheet, pressboard and mineral oil were utilized to catalyze the ageing process. This simulates the conditions existing in real time power transformers with its weight in the ratio of 1:1:10 [20]. Based on the thermal class of the mineral oil, the ageing temperature is to be chosen such that its operating temperature limit should be less than 10% of its flash point value. Hence, in the present study, the accelerated thermal ageing was carried out at 160°C in a temperature-controlled oven under air ambience. To study the effect of dibenzyl disulfide and silver sulfide, different concentrations of both the compounds were initially added in acetone and then mixed with the mineral oil. Acetone, being volatile, gets vaporized at higher temperatures. The sample composition used in the present research work is indicated in Table 1. The ageing was performed for a duration of 500 hours. To collect the aged pressboard specimens for analysis, five samples were removed from the oil at the same time in order to ensure the repeatability of experimental results.

B. SURFACE DISCHARGE ANALYSIS

Fig. 1 shows the experimental setup used for the surface discharge inception voltage measurement. High voltage AC was generated by a high-voltage amplifier (Trek 30/20 A) with the input control from a function generator (Tektronix AFG 3051 C). The surface discharge activity was studied using two chiseled stainless-steel electrodes because of the higher critical temperature involved in its phase transition.

TABLE 1. composition of sample used for thermal ageing.

Specimen	Code
Mineral oil	MO
Mineral oil + Ag_2S (50 ppm)	A1
Mineral oil + Ag_2S (100 ppm)	A2
Mineral oil + Ag_2S (200 ppm)	A3
Mineral oil + DBDS (100 ppm)	D1
Mineral oil + DBDS (500 ppm)	D2
Mineral oil + DBDS (1000 ppm)	D3

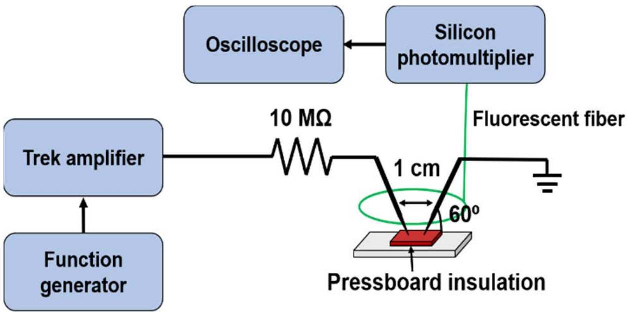

FIGURE 1. Schematic experimental setup used for surface discharge analysis.

The gap spacing between the two electrodes was maintained at 1 cm and these electrodes were inclined at an angle of 60° in order to increase the tangential electric field, which initiates the surface discharge phenomenon on the pressboard material as per IEC 60112 standard [21]. The pressboard material was connected to the high voltage electrode through a series resistance of 10 MΩ, while the other electrode was grounded. The plasma generated during the process of surface discharge was detected using a green fluorescent fiber (Saint Gobain Crystals BCF 91A) along with a highly sensitive photo detector. The fiber was looped around the electrodes where one end of the fiber was placed near the discharge gap length and the other end was fed to the silicon photomultiplier (SiPM) with maximum response at 430 nm [22] biased at 28 V. The emission characteristics of the fluorescence fiber and response of the SiPM module is overlapped making it compatible for the detection of surface discharge phenomenon. To avoid background light radiation, an opaque sleeve was used to cover the unexposed portion of the fiber, and the signals from the fluorescent fiber-based sensor was fed to the digital storage oscilloscope (3.5 GHz bandwidth, 40 GSa/s) with an input impedance of 50 Ω.

C. SURFACE POTENTIAL STUDIES

A needle-plane electrode arrangement was used to create the corona discharge, as illustrated in Fig. 2. A 10 kV DC supply voltage was generated by feeding the signal from the function generator through the Trek amplifier (Trek 20/20 C) for around 3 min. To measure the potential decay associated with the sample, the charge deposition from the corona discharge process was transferred from Position 1 to Position 2 on the sample surface. The gap separation maintained between the high voltage and ground was 3 mm. The capacitive Kelvin probe along with electrostatic voltmeter (Trek 341B) was used to quantify the surface potential associated with the pressboard material.

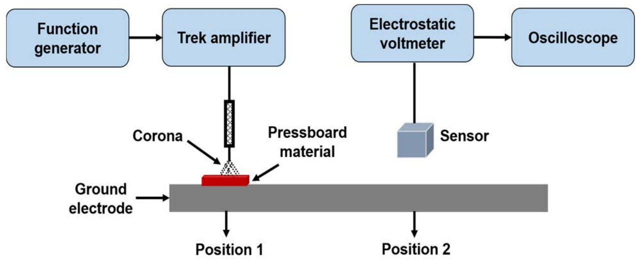

FIGURE 2. Schematic experimental setup used for surface potential measurement.

D. TENSILE STRENGTH

The pressboard material was tested using a Universal Testing Machine of 20 kN loading capacity with a displacement rate of 2 mm/min at room temperature to evaluate the ageing phenomenon. Tensile specimens in the dumbbell form with dimensions 115 mm × 6 mm × 3 mm, and a gauge length of 25 mm were sized according to ASTM D-638 (Type IV) [23]. Tests were carried out on four samples of the same pressboard material and averaged to ensure accuracy and reliability of the results. Digital image correlation (DIC) is an image-based approach for measuring shape, field displacement, and deformation at different points on the surface of the sample under examination. The DIC technique along with the tensile strength measurements was used to get the necessary displacements and strain information. Using a permanent marker pen and white paint over the sample surface, the specimen was speckled with black dots. A Grasshopper CCD camera (Sony ICX625 2/3′ sensor) of 5.0 MP with a maximum resolution of 2448 × 2048 pixels situated 50 cm in front of the universal testing equipment constantly recorded the displacement in the speckle pattern under tensile loading. The Canon lens that was utilized with the camera had a fixed focal length of 50 mm and during loading, an LED light source was used to brighten the speckle pattern on the sample surface while collecting the pictures. The Grasshopper GRAS-50S5 IEEE-1394b graphical user interface was used to capture the pictures, which were then saved in the computer. The collected digital pictures were post-processed and then analysed using Correlated Solutions Inc.'s VIC-2D software.

E. LASER INDUCED BREAKDOWN SPECTROSCOPY

The laser induced breakdown spectroscopy (LIBS) instrument consists of a Q switched Nd^{3+}: YAG laser

(LAB15010S2K, QuantaRay LAB series, Spectra Physics) to generate a 10 ns pulsed beam with a 10 Hz repetition rate [24]. A lens, with a focal length of 25 cm, was used to focus the laser on the pressboard surface, and once the laser's energy exceeded the material's threshold fluence, the optically induced plasma was ignited. Prior to LIBS testing, the thermally aged pressboard material was degreased with acetone to remove the mineral oil impregnated on its surface. In the present study, the laser was operated at an energy of 40 mJ and then focused at 90° to the pressboard material in order to create a spot of 0.5 mm diameter. The high-energy density laser pulse excites the atoms in the material to produce the plasma on the surface of pressboard specimen. With the information retrieved from optical emission during its transitions from the excited state to ground state, the elements present in the pressboard material is identified. The optical emission from the pressboard surface was captured at an angle of 30° by a lens with a focal length of 100 mm, which was then connected to an optical fiber.

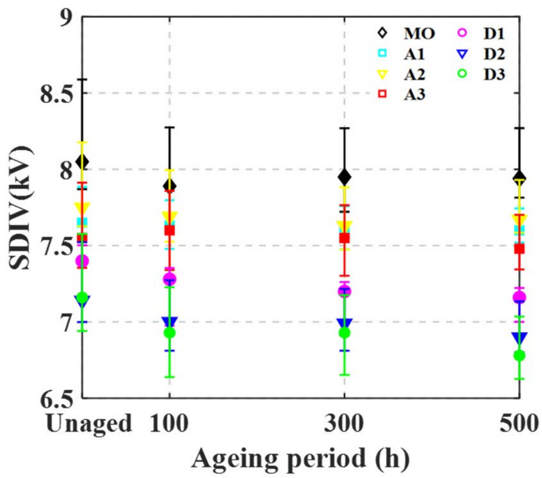

FIGURE 3. Variation in SDIV of thermally aged pressboard material with ageing time.

III. RESULTS AND DISCUSSIONS

A. SURFACE DISCHARGE INCEPTION VOLTAGE

The surface discharge inception voltage (SDIV) was measured based on the first discharge detected by the fluorescent fiber. The SDIV values of thermally aged mineral oil impregnated pressboard material under AC voltages for different concentrations of DBDS and Ag_2S with varying ageing time period are shown in Fig. 3. The SDIV was calculated for an average of 25 observations, and the standard deviation in the experimental results were found to be less than 0.5 kV. Once the first discharge is initiated upon the application of AC high voltage, there is a higher chance for the surface charges to remain on the pressboard's surface, which enhances the localised electric field and thus leads to subsequent discharges [25]. The SDIV is higher for mineral oil impregnated pressboard (MO) that was aged in the absence of DBDS and Ag_2S. Moreover, with an increase in the ageing time period to around 500 hours, a marginal decrease was noticed for all the samples. At higher ageing temperatures, the cellulose strands on the surface of the pressboard material breaks and these chain scissions can serve as charge trap sites [26], allowing more surface charge to accumulate on its surface. This causes the surface discharge activity to occur at lower voltages.

The lower concentrations of silver sulfide (A1, A2) and DBDS (D1) in mineral oil did not have much influence on the SDIV of the thermally aged pressboard material. This indicates that the diffusion of Ag_2S and DBDS from mineral oil towards the cellulosic pressboard is not much severe for concentrations upto 100 ppm, showing only a minimal change in its discharge magnitude. On the contrary, the SDIV of aged mineral oil impregnated pressboard material exhibited a marginal reduction of about 10% for 200 ppm of Ag_2S (A3) concentration and 15% for 1000 ppm of DBDS (D3) concentration. Flora *et al.* have concluded that lower concentrations of DBDS in mineral oil can increase the oxidation stability reducing the ageing process, and higher concentration levels could lead to a major hazard for the transformer insulation [27]. The results are in accordance with the previous research works, and it can be concluded that the degradation of the pressboard material occurs only for higher concentrations of DBDS. The copper sulfide species is not only formed in the windings of the transformer but it can also diffuse towards the surface of pressboard material forming a corrosive layer. The higher conductive nature of copper sulfide and silver sulfide compounds in mineral oil along with the ageing process can lead to various acidic derivatives in the oil forming a conductive channel on the pressboard material. This causes a drastic reduction in the magnitude of SDIV [28]. Comparing the effect of Ag_2S and DBDS on the ageing of mineral oil impregnated pressboard material, the SDIV was lower for DBDS aged specimen. The retardation of Ag_2S towards corrosive layer formation on the pressboard material can be a possible reason for its higher SDIV compared to that in the presence of DBDS. Fig. 4a shows a typical fluorescence signal pattern formed during the surface discharge activity, and the Fast Fourier Transform (FFT) of these fluorescence signals for the unaged and aged specimens is shown in Fig. 4b. Regardless of the condition under which the mineral oil impregnated pressboard material was aged, the bandwidth of the fluorescence signal lies in the range of 0-20 MHz.

B. SURFACE POTENTIAL AND TRAP CHARACTERISTICS OF AGED PRESSBOARD MATERIAL

1) SURFACE POTENTIAL DECAY

The surface potential decay of thermally aged pressboard material over time is shown in Fig. 5. The measured experimental results of surface potential ($V(t)$) was fitted using an exponential function as shown in Equation (1).

$$V(t) = V_0 \times e^{-\lambda t} \tag{1}$$

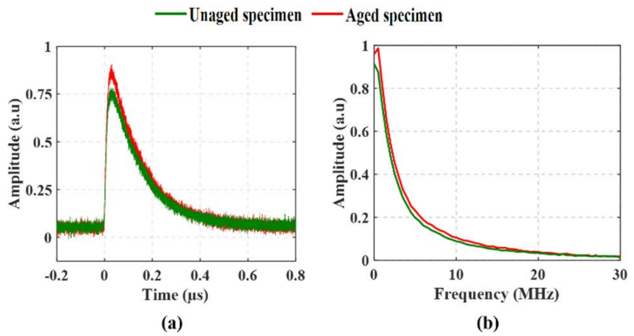

FIGURE 4. (a) Typical fluorescence signal due to surface discharge activity and (b) Fast Fourier Transform (FFT) of the fluorescence signal for unaged and thermally aged pressboard samples.

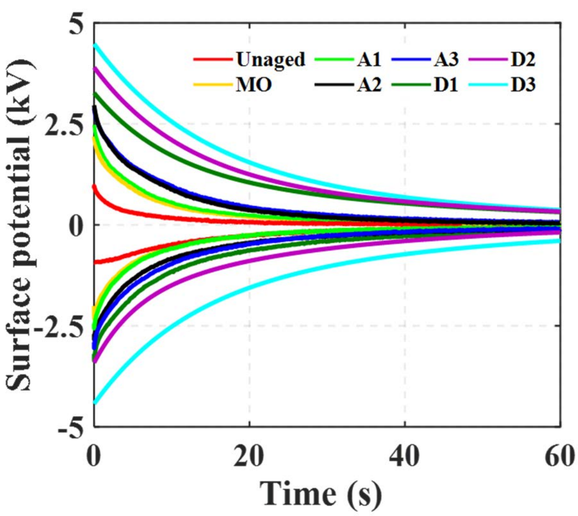

FIGURE 5. Variation of surface potential decay with respect to time.

where V_0 indicates the initial potential at t=0 s, λ is the decay rate and t is time in seconds. The potential of a thermally aged sample is observed to be greater than that of unaged sample. The charges deposited on the pressboard material under positive DC is higher than negative DC which is reflected in its initial potential magnitude as shown in Table 2. A higher potential of about 4.482 kV is observed for the pressboard aged with mineral oil containing DBDS (D3), which is almost 1.5 times higher than the pressboard aged in the presence of Ag_2S (A3). A similar trend in the potential decay is noticed under both positive DC and negative DC voltages for all the aged pressboard materials. This confirms that polarity has a negligible influence on the surface potential characteristics of thermally aged mineral oil impregnated pressboard material with DBDS and Ag_2S.

The half lifetime as shown in Table 2 is defined as the time taken for the surface potential accumulated on the pressboard specimen to reach 50% of its initial value. It is observed that the half lifetime is very low for the unaged samples compared to aged ones. Moreover, the pressboard aged with the dissolution of DBDS in mineral oil has shown a higher

TABLE 2. Parametric evaluation of pressboard specimens from surface potential measurements.

Specimen	Initial potential (V)		Half lifetime (s)	
	+DC	-DC	+DC	-DC
Unaged	960	-922	2.20	3.78
MO	2472	-2317	3.36	3.71
A1	2478	-2372	3.42	5.51
A2	2960	-2835	4.38	5.63
A3	3267	-3022	4.77	6.59
D1	3679	-3258	10.88	8.24
D2	3899	-3339	11.32	10.58
D3	4482	-4430	12.48	12.24

half lifetime compared to that in the presence of Ag_2S. This indicates that pressboard aged with DBDS leads to a higher potential magnitude with a lower decay rate compared to its ageing under varying concentrations of Ag_2S. The reason for the above change in the surface potential is the higher conductive nature of pressboard material due to the diffusion of DBDS [29] resulting in higher degradation of the cellulosic pressboard material compared to its effect with the addition of Ag_2S. These results are in agreement with the surface discharge analysis, and could be used as an alternative technique to comment on the early detection of incipient discharges.

2) TRAP DISTRIBUTION ANALYSIS

Fig. 6 shows the trap distribution of aged pressboard material which was calculated based on Simmon and Tam's theory. According to the literature, it is concluded that found that trap density can be related to tdV/dt [30], and there could be two peaks (shallow trap and deep trap) linked with the degradation. The trap density (N_t) and its demarcation energy (E_t) involved in the decay process are calculated as follows:

$$N_t = \frac{4\varepsilon_o \varepsilon_r}{eL^2kT}\left| t\frac{dV}{dt} \right| \quad (2)$$

$$E_t = kT.ln(\nu t) \quad (3)$$

where ε_o is the free space permittivity (8.854×10^{-12} F/m), ε_r is the pressboard material's dielectric constant, e is the electron charge (1.602×10^{-19} C), L is the thickness of pressboard specimen, k is the Boltzmann constant (1.38×10^{-23} m^2 kg s^{-2} K^{-1}), ν is the electron's escape frequency (10^{12} Hz) and T is the temperature.

The trap characteristics of aged pressboard material under both positive and negative DC did not exhibit any shallow traps whereas deeper traps were seen with trap energy in the range of 0.93 eV to 0.95 eV. According to Du *et al.* [31], a change in the trap demarcation energy towards higher values can be related to an increase in the time constant of voltage dissipation owing to an increase in trap density/trap depth. Only a minimal change in the trap energy is observed in this study, which shows a similar trap density magnitude for the pressboard material aged with both DBDS and Ag_2S addition in mineral oil. Thus, it has been understood the Cu_2S and Ag_2S diffusion into the pressboard material involves only deep traps with not much variation in its trap distribution.

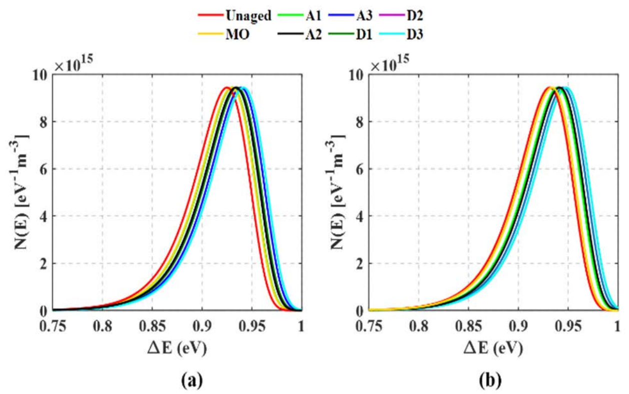

FIGURE 6. Trap distribution of aged pressboard specimens under (a) positive and (b) negative voltage.

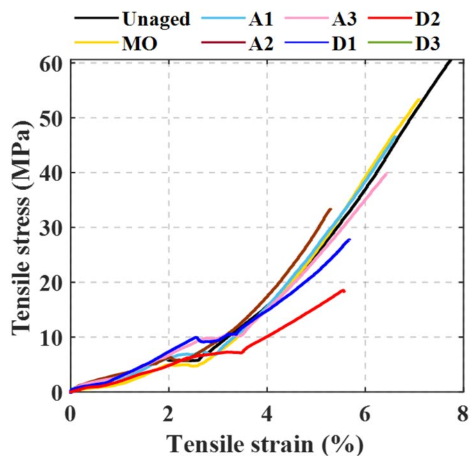

FIGURE 7. Tensile strength of thermal aged pressboard specimens.

C. EFFECT OF DBDS AND SILVER SULFIDE ON THE TENSILE PROPERTIES OF PRESSBOARD MATERIAL

Fig. 7 shows the tensile strength of thermally aged pressboard material (500 hours) impregnated with mineral oil containing both DBDS and Ag_2S. It is observed that unaged pressboard specimens withstand a higher tensile loading because of its increased degree of polymerisation. A marginal decrease has been noticed for the aged pressboard material confirming the disruption of only intermolecular hydrogen bonds present in the cellulosic structure [32]. On comparing the effect of thermal ageing on the pressboard material, the tensile strength was higher for the specimen MO followed by the pressboard aged at different concentrations of silver sulfide and DBDS. The sample with lower concentration of DBDS in mineral oil (D1) exhibited a tensile loading similar to that of higher concentrations of silver sulfide (A2). With thermal ageing, there occurs a reduction in the crystallinity and the effect of Cu_2S diffused into the pressboard material. The action of DBDS-Cu complex on cellulose can result in the breakage of D-glucopyranose units [33] present in the cellulosic chains, which reduces the tensile strength. On the contrary, the addition of Ag_2S would have resulted in much lesser chain scissions than the effect of Cu_2S towards the pressboard material, which results in higher tensile strength.

The tensile parameters of thermally aged pressboard specimens are shown in Table 3. The input load responsible for the deformation of pressboard is higher for the unaged sample followed by the ageing performed without the addition of DBDS and Ag_2S in MO. The reduction in load associated with the specimen MO was only 2.2% than the unaged specimen indicating its higher retardation towards the thermal ageing. The lower concentration of silver sulfide in mineral oil (A1) also showed only a minimal reduction in tensile strength of around 4.8% with respect to the unaged specimen, which is related to its lesser diffusion towards the pressboard material. However, higher concentrations of silver sulfide in mineral oil showed a reduction of 12% and 34.5% for the samples A2 and A3, respectively, indicating its higher diffusivity and corrosiveness on the pressboard material.

TABLE 3. Tensile parameters of aged pressboard specimens.

Specimen	Load (N)	Young's modulus (MPa)
Unaged	1003	782.94
MO	981	770.50
A1	954	752.11
A2	883	702.88
A3	657	630.11
D1	771	665.62
D2	458	488.55
D3	389	333.87

The sample containing low concentration of DBDS in mineral oil (D1) showed a higher tensile loading than the samples containing high concentration of silver sulfide (A3). The mechanical strength of the pressboard material degrades depending on its degree of polymerisation as well as its resistance towards the corrosive deposition. From the tensile results, it is evident that low concentration of DBDS in mineral oil (D1) does not favor the chemical reaction of DBDS-Cu complex to result in corrosive Cu_2S formation on the pressboard layer. However, at high concentrations (D2, D3), the reduction in the tensile loading was around 54.3% and 61.2%, respectively, which could be related to its corrosive nature of the pressboard surface. The Young's modulus quantifies the relation between the tensile stress and strain in its linear elastic region. The deformation involved during the application of extension load was higher for the unaged specimen compared to aged pressboard samples. The higher modulus of the unaged pressboard material indicates a higher stress required for the strain deformation. The Young's modulus of the pressboard material can further be related to number of hydrogen bonds present per unit volume of the cellulosic structure [32]. This leads to the higher rupturing of polymeric chains present within the glycosidic units of cellulose pressboard for the diffusion of Cu_2S from mineral oil compared to its effect in presence of Ag_2S. To measure

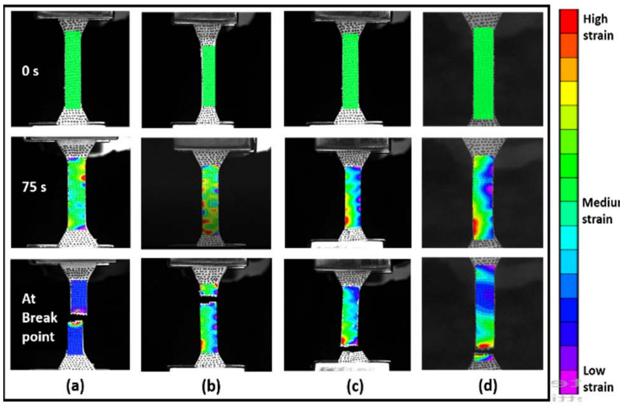

FIGURE 8. Strain contour variation of aged specimen (a) Unaged (b) MO, (c) A3 and (d) D3.

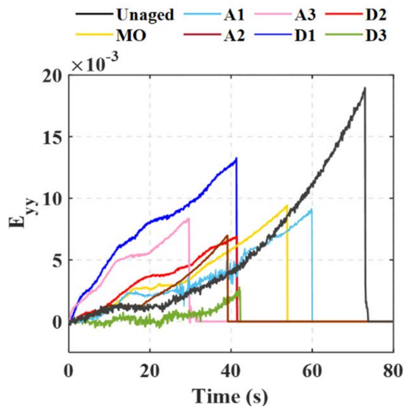

FIGURE 9. Elongation of specimen in y-direction at maximum strain.

the deformations occurring at distinct locations on the pressboard material, Digital Image Correlation (DIC) is adopted in the present work with variation in contour strain indicated in Fig. 8. The contour strain variation on the surface of pressboard material corresponds to the pressboard aged for 500 hours with high concentrations of DBDS and Ag_2S. Fig. 8 represents the typical DIC correlation images that were captured during the testing. The tensile stress and strain that were obtained from the experiment is correlated with the post image processing of the speckle images recorded simultaneously. The deformation of the pressboard material gets altered with respect to time and it showed a higher strain concentration region at the point of breakage.

Further, it is also important to realize the tensile strain variation over the gauge length of the test specimen, and hence the specific surface area is marked to visualize the elongation in the y direction (E_{yy}). The elongation (E_{yy}) plotted against the time (Fig. 9) shows a linear increment till the point of breakage. A higher elongation is observed for the unaged pressboard specimen with a longer time taken for its deformation. Followed by this, the time taken to achieve the breaking point is higher for specimen MO and A1. Although the tensile loading showed a marginal variation in the sample of DBDS and Ag_2S, the breaking point of specimens D1, D2, D3 and A1 lies around 40 s. It can be understood that elongation and breaking point do not provide correct information on the degradation associated with the pressboard material whereas strain contour identified through DIC analysis can be used to relate the degree of polymerization (DP) of pressboard insulation.

D. LASER INDUCED BREAKDOWN SPECTROSCOPY

The laser-induced breakdown spectroscopy (LIBS) has been adopted in the present work for identifying thermally aged pressboard samples by coupling the spectral elements with multivariate analysis. It has been concluded from our previous studies that increasing the delay period diminishes the strength of the elemental peaks and the pulsed laser's energy [24]. In the present work, the laser and the spectrometer were synchronized with the help of a control device in order to capture the emission of plasma generating the atomic spectra at the time of ablation. The elemental composition of thermally aged pressboard material obtained using LIBS is shown in Fig. 10a. The formation of prominent peaks of copper, carbon, silver and sulfur (Cu I, C II, Ag I, S II) was observed from the LIBS emission spectra along with the other elements such as nitrogen (N II) and oxygen (O I, O II), which could have been formed due to external environmental conditions of the experiment. The normalization of intensity was performed to compare the unaged and aged pressboard materials. The intensity of peaks corresponding to S II (563.9 nm, 757.89 nm), Ag I (757.89 nm), and Cu II (521.8 nm) were found to increase for the pressboard material aged with mineral oil containing DBDS and Ag_2S.

Assuming a local thermal equilibrium (LTE) in the area confined to the plasma plume during the collisions between the particles in the plasma species [34], the plasma temperature was calculated using the Boltzmann Saha equation as shown in the equation (4) and the emission lines were identified by comparing them with the NIST database [34].

$$T_e = 1.44 \left[\frac{E_2 - E_1}{\ln \left\{ \frac{I_1 \lambda_1 A_2 g_2}{I_2 \lambda_2 A_1 g_1} \right\}} \right] \tag{4}$$

where I_1 and I_2 are the intensities of the atomic species corresponding to excited energy levels E_1 and E_2 at wavelengths of λ_1 and λ_2, g_1 and g_2 are the statistical weights of excited energy level with transition probability states A_1 and A_2, respectively.

Among the different elements identified from the LIBS emission spectra, the elements of C II and S II were chosen for its calculation of plasma temperature as shown in Table 4. These elements were alone considered since they are responsible for the major degradation of the pressboard material. The plasma temperature is high for the unaged specimen indicating its higher strength with the strong glycosidic bonding involved in the cellulose structure. With ageing, the plasma temperature is lowered, which could be related to chemical breakdown of long polymeric chains of cellulose

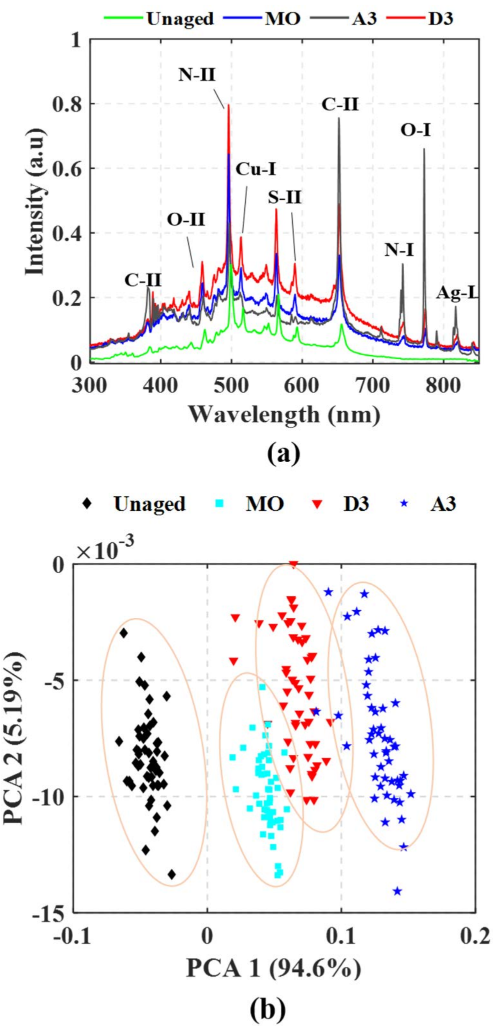

FIGURE 10. (a) LIBS emission spectra of thermally aged pressboard specimens, (b) Distribution of LIBS spectral database for the aged pressboard specimens.

TABLE 4. Plasma temperature of aged pressboard material.

Specimen	Plasma temperature (K)	
	C- II	S- II
Unaged	18680.54	34082.67
MO	17563.97	22101.45
A3	16844.13	20895.65
D3	15854.10	21427.05

into furanose isomers, anhydrous sugars, and low molecular weight oxygenates [30]. Moreover, it is to be noticed that specimens MO, A3 and D3 showed a marginal decrease in the plasma temperature compared to unaged specimen and hence it could be used as a quantitative parameter to differentiate the ageing involved due to DBDS and Ag_2S on the pressboard material.

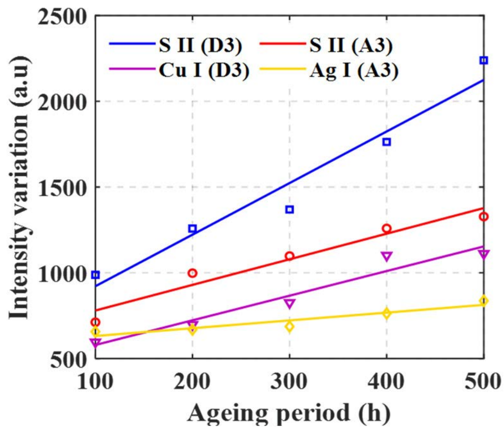

FIGURE 11. LIBS intensity variation with ageing period.

Furthermore, to identify and classify the aged pressboard specimens due to DBDS and Ag_2S diffusion from the unaged ones, the principal component analysis (PCA) of the LIBS emission spectra was adopted. Compared to our previous studies where the ageing conditions in the pressboard were classified based on the emission spectra throughout the wavelength range of 200-800 nm [24], the present work considers only the prominent peaks of Cu I, C II, S II and Ag I as input to PCA algorithm. Totally, 200 LIBS spectral data were given as input to the model out of which 50 spectra corresponds to each specimen. By considering only the selected peaks for the PCA model, it is possible to achieve a total variance of 99.8% with two principal components (PC1 (94.6%) and PC2 (5.19%)) as shown in Fig. 10b. It is observed that unaged pressboard specimens got separated from the aged specimens with a slight overlap occurring for aged specimens MO and D3. The specimen A3 can be distinguished from the other aged specimens because of the higher intensity of silver peak observed on the pressboard material with the diffusion of Ag_2S in mineral oil.

The diffusion of DBDS from the mineral oil towards copper sulfide formation on the pressboard material has still now been confirmed only with its elemental characterization. In the present work, the LIBS intensity of higher concentration of DBDS (D3) and Ag_2S (A3) added in mineral oil has been considered to understand its diffusion mechanism with respect to ageing time period as shown in Fig. 11. A linear variation in the intensities of S II, Cu I and Ag I is observed for the specimens D3 and A3 with ageing time providing a better correlation coefficient ($R^2 > 0.98$).

The rate of change in LIBS intensity with respect to time will be a very useful parameter to understand the diffusion of ions from the oil to the pressboard material. The change in intensity was two times higher for the sulfur ions in the specimen D3 (300.7) compared to specimen A3 (149.7), whereas the change in intensity of Cu I ions and Ag I were 143.6 and 45.1 for specimen D3 and A3. These confirm the higher degradation in pressboard material through the diffusion of Cu_2S due to the addition of DBDS than its impact with Ag_2S.

Thus, the LIBS intensity variation can be correlated with the existing diffusion parameters discussed in the earlier research works [36, 37] for its calibration and it could be used as an alternative technique by the insulation engineers for assessing the degradation of pressboard due to both DBDS and Ag_2S.

IV. CONCLUSION

- The SDIV of the aged pressboard material using fluorescent fiber technique showed a marginal reduction in its magnitude only for concentrations greater than 100 ppm of DBDS and 200 ppm of Ag_2S added in mineral oil.
- The parameters of fluorescence signal did not vary in terms of time scale and voltage amplitude with its bandwidth lying in the range of 0-20 MHz irrespective of ageing of the pressboard material.
- The aged pressboard specimens showed an increase in the surface potential for higher concentrations of DBDS compared to its effect with the addition of Ag_2S in mineral oil. In addition, only deep traps have been noticed with a constant trap density level for aged pressboard material with a slight right shift observed in its trap energy.
- The tensile strength decreased marginally for the pressboard material aged with DBDS compared to that in case of Ag_2S based system. Moreover, the percentage reduction in the tensile loading was seen to be higher for the DBDS aged pressboard specimen indicating its higher diffusion and corrosivity involved with the thermal ageing. The evaluation of strain at different places on the surface of the pressboard has been visualized using Digital Image Correlation (DIC) technique confirming the tensile measurement results.
- LIBS analysis indicates the presence of copper, carbon, sulfur and silver peaks in its emission spectra, which could be related to its ageing. Further, to classify the ageing of pressboard with regard to DBDS and Ag_2S addition in mineral oil, PCA technique was adopted indicating a clear overlap for the aged specimens.
- The intensity of Cu I, S II and Ag I followed a linear relation with respect to ageing duration. The rate of diffusion of sulfur on DBDS aged pressboard specimen was two times greater than its effect with the ageing performed on addition of Ag_2S. Thus, it is concluded that quantification of elements and intensity variation from the LIBS analysis could provide more insight on the diffusion of corrosive sulfur derivatives towards the insulating pressboard material.

REFERENCES

[1] A. Kuchler, "Insulating material," in *High Voltage Engineering*. Berlin, Germany: Springer-Vieweg, 2018, pp. 301–354.
[2] U. M. Rao, I. Fofana, T. Jaya, E. M. Rodriguez-Celis, J. Jalbert, and P. Picher, "Alternative dielectric fluids for transformer insulation system: Progress, challenges, and future prospects," *IEEE Access*, vol. 7, pp. 184552–184571, 2019.
[3] J. N'cho, I. Fofana, Y. Hadjadj, and A. Beroual, "Review of physicochemical-based diagnostic techniques for assessing insulation condition in aged transformers," *Energies*, vol. 9, p. 367, May 2016.
[4] G. Kaliappan and M. Rengaraj, "Aging assessment of transformer solid insulation: A review," *Mater. Today, Proc.*, vol. 47, pp. 272–277, May 2021.
[5] H. Cong, M. Zhang, X. Shu, and Q. Li, "Protective performance of different passivators on oil-paper insulation containing multiple corrosive sulphides," *IEEE Access*, vol. 7, pp. 4083–4090, 2019.
[6] T. Amimoto, E. Nagao, J. Tanimura, S. Toyama, Y. Fujita, H. Kawarai, and N. Yamada, "Identification of affecting factors of copper sulfide deposition on insulating paper in oil," *IEEE Trans. Dielectr. Electr. Insul.*, vol. 16, no. 1, pp. 265–272, Feb. 2009.
[7] J. J. Erbrink, E. Gulski, J. J. Smit, P. P. Seitz, B. Quak, R. Leich, and R. A. Malewski, "On-load tap changer diagnosis-an off-line method for detecting degradation and defects—Part 1," *IEEE Elect. Insul. Mag.*, vol. 26, no. 5, pp. 49–59, Oct. 2010.
[8] S. Samarasinghe, H. Ma, C. Ekanayake, D. Martin, and T. Saha, "Investigating passivator effectiveness for preventing silver sulfide corrosion in power transformer on-load tap changers," *IEEE Trans. Dielectr. Electr. Insul.*, vol. 27, no. 5, pp. 1761–1768, Oct. 2020.
[9] J. S. Rajan, S. D. Flora, and C. Ranganathaiah, "Investigations of copper sulfide diffusion into paper insulation of transformers," *IEEE Trans. Dielectr. Electr. Insul.*, vol. 23, no. 4, pp. 2421–2429, Aug. 2016.
[10] F. Scatiggio, V. Tumiatti, R. Maina, M. Tumiatti, M. Pompili, and R. Bartnikas, "Corrosive sulfur induced failures in oil-filled electrical power transformers and shunt reactors," *IEEE Trans. Power Del.*, vol. 24, no. 3, pp. 1240–1248, Jul. 2009.
[11] P. Jusner, E. Schwaiger, A. Potthast, and T. Rosenau, "Thermal stability of cellulose insulation in electrical power transformers—A review," *Carbohydrate Polym.*, vol. 252, Jan. 2021, Art. no. 117196.
[12] S. Thakur, R. Sarathi, R. Gautam, and R. Vinu, "Thermal aging of cellulosic pressboard material and its surface discharge and chemical characterization," *Cellulose*, vol. 24, no. 11, pp. 5197–5210, Nov. 2017.
[13] W. Sikorski, "Development of acoustic emission sensor optimized for partial discharge monitoring in power transformers," *Sensors*, vol. 19, no. 8, p. 1865, Apr. 2019.
[14] G. V. R. Xavier, H. S. Silva, E. G. da Costa, A. J. R. Serres, N. B. Carvalho, and A. S. R. Oliveira, "Detection, classification and location of sources of partial discharges using the radiometric method: Trends, challenges and open issues," *IEEE Access*, vol. 9, pp. 110787–110810, 2021.
[15] S. Murugesan, A. J. Amalanathan, R. Sarathi, B. Srinivasan, and R. Samikannu, "Investigation on impact of magnetic field on the corona discharge activity in Punga oil using fluorescent fiber and UHF sensor techniques," *IEEE Access*, vol. 9, pp. 129218–129228, 2021.
[16] I. A. Carrascal, C. Fernaández-Diego, J. A. Casado, S. Diego, I. Fernaández, and A. Ortiz, "Quantification of Kraft paper ageing in mineral oil impregnated insulation systems through mechanical characterization," *Cellulose*, vol. 25, no. 6, pp. 3583–3594, 2018.
[17] G. K. Frimpong and L. Melzer, "Evaluation of mechanical condition of transformer paper insulation after factory drying," *IEEE Elect. Insul. Mag.*, vol. 35, no. 6, pp. 23–32, Nov. 2019.
[18] R. Noll, "Laser-induced breakdown spectroscopy," in *Laser-Induced Breakdown Spectroscopy*. Berlin, Germany: Springer, 2012, pp. 7–15.
[19] *Pressboard and Presspaper for Electrical Purposes—Part 2: Methods of Tests*, document Rec. IEC 60641-2, 2004.
[20] K. Bandara, C. Ekanayake, T. K. Saha, and P. K. Annamalai, "Understanding the ageing aspects of natural ester based insulation liquid in power transformer," *IEEE Trans. Dielectr. Electr. Insul.*, vol. 23, no. 1, pp. 246–257, Feb. 2016.
[21] *Method for the Determination of the Proof and the Comparative Tracking Indices of Solid Insulating Materials*, document Rec. IEC 60112, 2020.
[22] G. D. P. Mahidhar, R. Sarathi, and B. Srinivasan, "Fluorescence fiber based identification of partial discharges in liquid nitrogen for high-temperature superconducting power apparatus," *IEEE Sensors Lett.*, vol. 4, no. 2, pp. 1–4, Feb. 2020.
[23] N. Chillu, R. Jayaganthan, R. Velmurugan, and R. Sarathi, "Investigation on the digital image correlation and charge trap characteristics of Al/epoxy nanocomposites," *Mater. Res. Exp.*, vol. 7, no. 2, Feb. 2020, Art. no. 025035.
[24] A. J. Amalanathan, N. J. Vasa, N. Harid, H. Griffiths, and R. Sarathi, "Classification of thermal ageing impact of ester fluid-impregnated pressboard material adopting LIBS," *High Voltage*, vol. 6, no. 4, pp. 655–664, Aug. 2021.
[25] X. Yi and Z. Wang, "The influences of solid surface on the propagation of creepage discharge in insulating liquids," *IEEE Trans. Dielectr. Electr. Insul.*, vol. 22, no. 1, pp. 303–312, Feb. 2015.

[26] M. Huang, Y. Zhou, C. Dai, W. Chen, L. Lu, and Y. Sha, "Charge transport in thermally and electrically stressed oil-impregnated paper insulation," *IEEE Trans. Dielectr. Electr. Insul.*, vol. 23, no. 1, pp. 266–274, Feb. 2016.
[27] 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.
[28] A. N. N. J. Vasa, R. Vinu, and R. Sarathi, "Influence of ambient medium on thermal ageing of pressboard in transformer oil containing dibenzyl bisulphide (DBDS)," *IEEE Trans. Dielectr. Electr. Insul.*, vol. 24, no. 5, pp. 2836–2846, Oct. 2017.
[29] J. Zhou, Y. Yuan, G. Liu, and C. Zhang, "The effects of corrosive sulfur in bushing: Corrosion of aluminum foil and its effect of oil-paper insulation," *IEEE Access*, vol. 7, pp. 143735–143741, 2019.
[30] A. J. Amalanathan, R. Sarathi, N. Harid, H. Griffiths, R. Gautam, and R. Vinu, "Investigation on the performance of thermally aged natural ester fluid impregnated pressboard material," *IEEE Trans. Dielectr. Electr. Insul.*, vol. 27, no. 5, pp. 1578–1586, Oct. 2020.
[31] B. X. Du, J. P. Jiang, J. G. Zhang, and D. S. Liu, "Dynamic behavior of surface charge on double-layer oil-paper insulation under pulse voltage," *IEEE Trans. Dielectr. Electr. Insul.*, vol. 23, no. 5, pp. 2712–2719, Oct. 2016.
[32] L. Naranpanawe, C. Ekanayake, and T. K. Saha, "Measurements on pressboard to understand the effect of solid insulation condition on monitoring of power transformer winding clamping pressure," *IET Sci., Meas. Technol.*, vol. 13, no. 2, pp. 186–192, Mar. 2019.
[33] R. J. Liao, C. Tang, L. J. Yang, and S. Grzybowski, "Thermal aging microscale analysis of power transformer pressboard," *IEEE Trans. Dielectr. Electr. Insul.*, vol. 15, no. 5, pp. 1281–1287, Oct. 2008.
[34] A. Descoeudres, C. Hollenstein, R. Demellayer, and G. Wälder, "Optical emission spectroscopy of electrical discharge machining plasma," *J. Phys. D, Appl. Phys.*, vol. 37, no. 6, p. 875, 2004.
[35] J. E. Sansonetti and W. C. Martin, "Handbook of basic atomic spectroscopic data," *J. Phys. Chem. Reference Data*, vol. 34, no. 4, pp. 1559–2259, Dec. 2005.
[36] S.-H. Gao, L.-J. Yang, and D. Ding, "Corrosion mechanism for copper sulfide formation induced by dibenzyl disulfide in oil-immersed insulation," *IEEE Access*, vol. 7, pp. 23100–23108, 2019.
[37] S. Samarasinghe, H. Ma, D. Martin, and T. Saha, "Investigations of silver sulfide formation on transformer OLTC tap selectors and its influence on oil properties," *IEEE Trans. Dielectr. Electr. Insul.*, vol. 26, no. 6, pp. 1926–1934, Dec. 2019.

S. K. AMIZHTAN is currently a Research Scholar with the Department of Electrical Engineering, IIT Madras, Chennai, India. His research interests include condition monitoring and characterization of nanofluid-based transformer insulation.

A. J. AMALANATHAN is currently a Research Scholar with the Department of Electrical Engineering, IIT Madras, Chennai, India. His research interests include condition monitoring of ester and its nanofluids for power transformers.

R. SARATHI (Senior Member, IEEE) is currently a Professor and the Head of the High Voltage Laboratory, Department of Electrical Engineering, IIT Madras, Chennai, India. His research interest includes condition monitoring of power apparatus and nanomaterials.

R. VINU is currently an Associate Professor with the Department of Chemical Engineering, IIT Madras, Chennai, India. His research interests include characterization of polymer and hydrocarbon oil degradation, resource recovery from polymers via from thermochemical conversion techniques, and biomass conversion to biofuels and fine chemical intermediates.