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Understanding the influence of ambience on thermal ageing of natural ester liquid

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Abstract: Ambience during thermal ageing of ester liquid has a high impact on corona inception voltage (CIV) under AC and DC voltages. The CIV is high with ester liquid thermally aged in nitrogen ambience and is the least with air aged. CIV is high under negative DC voltage followed by positive DC and AC voltages. CIV reduces with increase in harmonic voltage and the reduction is predominant with harmonic voltages with higher total harmonic distortions. Corona activity radiates ultra-high-frequency (UHF) signal with its dominant frequency at 1 GHz. Phase-resolved partial discharge analysis carried out using UHF signal indicates that corona discharges occur at the peak of the voltage waveform. The magnitude of discharges is less in thermally aged liquid but the number of discharges increases. Fourier transform infrared spectroscopy analysis indicates the formation of carbonaceous particles with thermal ageing. Thermal ageing of ester liquid causes to form new chromophoric moieties causing red shift of absorption band in ultraviolet–visible spectra. Fluorescence spectroscopy traces the characteristic variations due to thermal ageing, which can be adopted for condition monitoring.

1 Introduction

Transformer is the key component in the power system network and its reliability relies on proper insulation design. Mineral oil has been widely used as an insulant in transformers. However, due to their toxic and hazardous nature, extensive work is being carried out considering environmentally compatible ester liquids as an alternative to mineral oils [1, 2]. Many researchers have explored the possibility of using an optimum mixture of mineral oil and ester liquid in order to attain desirable dielectric strength [3, 4]. Compared to mineral and silicone liquids ester liquids show higher flash, fire point, higher dielectric strength as well as higher biodegradability [5]. Research has also shown that addition of nanoparticles in ester liquid can further enhance its physical and electrical properties [6].

The insulation in a transformer undergoes multi-stress (such as thermal, electrical and chemical stress simultaneously), during its operation. In recent times, the power electronics and non-linear loads cause distortion to supply voltages, which can cause severe stress to transformer insulation, thereby reducing the life of transformer insulation. Another major problem which can cause severe damage to the transformer insulation (transformer oil and the pressboard material) is due to hot spot formation, where the local temperature can rise more than 110°C. This hot spot temperature can cause chemical damage to the oil causing carbonisation and acid formation in oil. Hence, the thermal ageing studies need to be carried out to understand the performance of natural ester liquid. Jeong *et al.* [7] on carrying out accelerated thermal ageing studies with vegetable oil and mineral oil have concluded that vegetable oil has better characteristics for insulation after thermal ageing but due to poor heat transfer characteristics arising from high kinematic viscosity, the pressboard material in aged vegetable oil degrades faster. Reffas *et al.* have studied influence of thermal ageing of olive oil and indicated reduction in dielectric constant, dissipation and flash point accompanied by an increase in acid number, viscosity and resistivity of the liquid. They also have indicated that the colour index of olive oil on thermal ageing lies between 1.3 and 1.5 [8].

During design and testing of transformers, discharges such as corona developed from a weak link like the edge of the winding or due to a protrusion from the winding conductor tend to cause major problems [9, 10]. It has been observed that ultra-high-frequency (UHF) signals are radiated by incipient discharges in transformer insulation [11]. Also, due to thermal ageing, the characteristic changes that occur in natural ester liquid, in different ambience [air, nitrogen (N_2) and helium (He)] corona inception voltage (CIV), need to be observed and analysed. In addition, the characteristic of UHF signal formed in thermally aged natural ester liquid needs to be understood.

Mineral oil is a complex mixture of a large number of hydrocarbons. The oils show intrinsic fluorescence properties due to the presence of polycyclic aromatic hydrocarbons, which breakdown with ageing, to form polar oxygenated molecules which result in loss of fluorescence [12]. Degradation of insulating liquid due to ageing leads to loss of dielectric strength, which is reflected by reduced breakdown strength of aged mineral oil. Three factors: temperature, oxygen availability and catalyst presence influence the chemical stability of oil in the transformer. Reports suggest the presence of oxygen may cause a rise in acidity number and leads to sludge formation [13].

Fourier transform infrared spectroscopy (FTIR) is a reliable technique to identify changes in any functional groups variations due to thermal ageing. Hadjadj *et al.* [14] have used FTIR and ultraviolet–visible (UV–Vis) spectrophotometric measurements to characterise the insulating oil decaying process; they correlated the FTIR absorbance of insulating oil with dissolved decay products formed in insulating oil. An extraction method coupled with FTIR analysis is used by Georgiev *et al.* [15] to characterise the main oxidation products formed in transformer oils.

UV–Vis spectrophotometry and IR spectroscopy have been used extensively toward monitoring the changes taking place in oil sample during the course of accelerated ageing. Karmakar *et al.* [16] have used UV–Vis spectroscopy to characterise the degradation of transformer oil due to combination of ageing processes (such as partial discharge, electrical arcing and thermal ageing); they have observed that aged transformer oil exhibits optical absorption in the range 200–400 nm. It is further established that with progressive ageing, the proportionate degradation of transformer oil is related to UV–Vis spectral data [17].

Fluorescence spectroscopy is a powerful technique to monitor and characterise the ageing of oils, due to its high sensitivity and

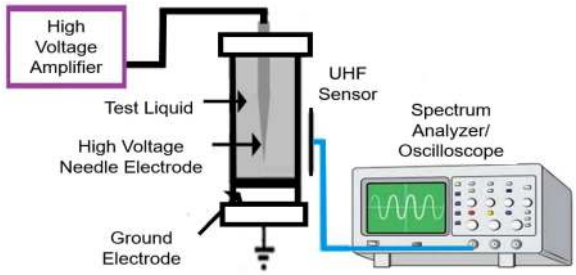

Fig. 1 *Experimental setup for CIV measurement*

selectivity. Natural ester liquid is primarily extracted from vegetable and seeds which are rich sources of fluorescent substances such as pheophytins, tocopherols, poly-phenolic compounds, saturated and unsaturated fatty acids, vitamin E and its derivatives, linoleic acid and other vitamins [18]. Unsaturated fatty acids with conjugated double bond exhibit fluorescence emission at around 415 nm [19]. Synchronous fluorescence spectroscopy and excitation–emission matrix fluorescence (EEMF) techniques have been used to monitor the ageing-related fluorescence spectral changes of mineral oil [20]. At high temperature, molecular level changes take place in oil [21]: (i) in the presence of moisture, the ester linkage undergoes hydrolysis; (ii) due to the action of air, oxidative degradation of oil takes place; (iii) homolytic cleavage of carbon–carbon or carbon–hydrogen bond takes place. Smaller free radicals (such as hydrogen, methyl and ethyl) are relatively stable; larger free radicals breakdown to form smaller, more stable radicals and other unsaturated olefin compounds. The free radicals are reactive and they undergo chain reactions to form lighter lower boiling unsaturated compounds, gases and additional free radicals.

Having known this, an attempt has been made to characterise and correlate the physicochemical changes occurring due to different ambiences during thermal ageing of natural ester liquid. The following analysis is done in the present study: (i) variation in CIV of natural ester liquid thermally aged in different ambiences, under AC, DC and harmonics distorted AC voltages. (ii) UHF signal formed due to corona activity in thermally aged natural ester liquid. (iii) Phase-resolved partial discharge (PRPD) analysis of aged oil. (iv) UV–Vis and fluorescent spectroscopic techniques to trace the molecular level changes in natural ester liquid due to thermal ageing.

2 Materials and methods

2.1 Thermal ageing

2.1.1 Sample preparation: In the present paper, thermal ageing of natural ester liquid (FR3 Envirotemp procured from Cargill India Pvt. Ltd.) is carried out at 110°C. Materials such as copper and oil impregnated pressboard (OIP, procured from Andrew Yule Pvt. Ltd.) were added in weight ratio of 1:1:10 (copper: OIP: test liquid) during ageing period. The pressboard samples were preheated in test liquid for 6 h at 100°C to remove traces of moisture and ensure uniform impregnation of oil.

2.1.2 Thermal ageing setup: The oil samples in top covered glass jar added with copper and pressboard material is placed on a thermostatically controlled heater for 21 days (500 h). Thermal ageing was carried out as per standard (IEEE c57.100) adopted for mineral oil [22]. The unfilled zone in the glass jar was provided with the suitable ambience of N_2/He by continuous purging of gas in the vessel at controlled atmospheric pressure to ensure a uniform blanket of gas over the oil. Air ambience ageing was carried out in a hot air oven at controlled temperature. The purpose of He and N_2 gas is to limit the influence of oxygen content during ageing process. The oil samples along with materials of equal above specified ratio were taken out at regular intervals of 24 h for analysis. In the discussion, virgin sample is referred as Type A, 21 days aged oil in the N_2, He and air medium are referred as Type B, Type C and Type D, respectively.

2.2 Experimental setup

2.2.1 Corona analysis: CIV of thermally aged ester liquid was calculated using the test setup shown in Fig. 1. The setup comprises of three parts: (i) the high-voltage source, (ii) test cell and (iii) the UHF sensor along with spectrum analyser/digital storage oscilloscope (DSO).

The AC, DC and harmonic AC voltage with different total harmonic distortions (THDs) were generated by using a high-frequency amplifier, with its input signals obtained from the function generator. The generated high AC voltage was measured by using a capacitive divider (V_{rms}). For harmonic voltages, peak factor was used to obtain exact root-mean-square values. The voltage was increased to the required level, at a rate of 300 V/s.

In the current analysis, a test cell of capacity 80 ml with needle and plane electrode made of stainless steel is used. To avoid the impact of micro-erosion of the tip on occurrence of corona activity, the needles were changed after every five readings. Needle–plane electrode configuration was used for generation of corona in the test cell. The radius of curvature of the needle electrode is about 50 µm. The ground electrode is a plane electrode of 5 cm diameter. The gap between the needle and ground electrodes was maintained at 5 mm.

A high-frequency DSO (Lecroy Model Wavepro 4 channel digital real-time oscilloscope, 3.5 GHz bandwidth, operated at 40 GSa/s) with an input impedance of 50 Ω and spectrum analyser Agilent CX-9000 was used for storing and analysing the UHF signal. The UHF sensor was kept 20 cm away from the test cell. The output of the UHF sensor is connected to the high bandwidth DSO or to the spectrum analyser.

2.2.2 UV–Vis analysis: Electronic absorption spectra were measured with a Shimadzu V-2500 A1 UV–Vis spectro-photometer with a scan rate of 1000 nm s^{-1}. About 1 mm path length cuvettes were used in order to avoid excessive absorbance of light in the liquid matrix. Hexane was chosen as a solvent for baseline correction during UV–Vis spectral measurements.

2.2.3 Fluorescence spectroscopy: Fluorescence measurements were performed with a Horiba Jobin Yvon spectrofluorometer (Fluoromax-4) with a xenon lamp of 150 W. A triangular cuvette was used in order to obtain both front and back-face fluorescences with minimum scattering. Excitation and emission monochromator band passes were kept at 1 nm. EEMF spectra were measured in the excitation wavelength range of 300–500 nm with an interval of 10 nm and in the emission wavelength range of 350–700 nm with an interval of 2 nm. All fluorescence measurements of the oil samples were taken at a regular interval of 24 h until 21st day. The instrumental drift and variation in lamp intensity were monitored periodically. Both the lamp intensity measured using a photodiode and the water Raman spectra (excited at 350 nm) shows very minimal instrumental changes over the experimental time span. Any instrumental changes could have required further suitable standardisation to correct fluorescence spectra before analysis. Since no significant variation was observed both in lamp profile and water Raman spectra, no further standardisation was adopted and the spectra were analysed as such.

2.2.4 Viscosity and FTIR analysis: Viscosity measurements were performed on an Anton Paar's modular compact rheometer 102, with a CP 40 cone and plate measuring system. The calibration of the instrument was done using a standard fluid (Wacker silicone fluid) provided by the instrument manufacturer. All ester liquid samples kept under high vacuum were allowed to equilibrate for 10 min before the start of the experimental studies. The experimental temperature was controlled by P-PTD 200/AIR plate–Peltier temperature device. FTIR measurements were done with a Jasco IR spectrometer (FTIR-4100) in the range 400–4000 cm^{-1}. Sodium chloride disc pallets were chosen during baseline correction.

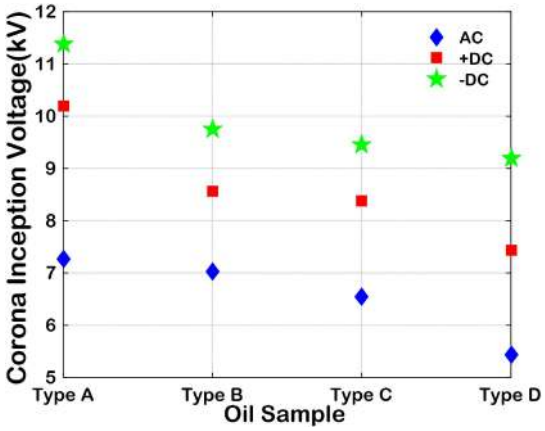

Fig. 2 *Variation in CIV of Type A, Type B, Type C and Type D liquid under AC, + DC and −DC voltages*

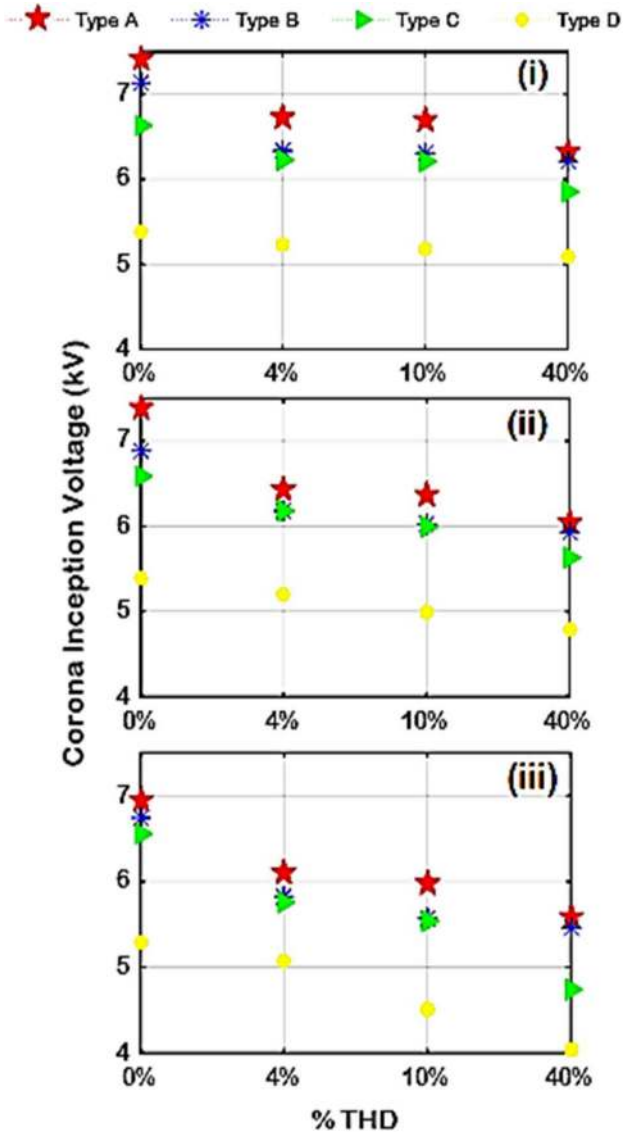

Fig. 3 *Variation of CIV with respect to different THDs for oil samples for (i) 3f harmonics, (ii) 5f harmonics, and (iii)7f harmonics*

3 Results

3.1 Analysis of CIV variation under different voltage profiles

Fig. 2 shows the variation in CIV of thermally aged ester liquid in different ambiences. On application of high voltage to the needle–plane electrode gap, the voltage at which the first inception of corona activity is observed through UHF sensor signal output observed in the oscilloscope is taken as the CIV. It is observed that CIV is the least under AC voltage and the highest under negative DC voltage. Reduction in CIV is observed in thermally aged ester liquid. This is seen to be predominant when the liquid is aged in air medium compared with ageing in He/N_2 ambience and ester liquid aged in N_2 ambience observed to have a more blanketing effect. Gockenbach *et al.* have reported that there is a significant decrease in partial discharge inception voltage of thermally aged naphthenic mineral oil [23]. Cavillini *et al.* have also studied the effect of thermal ageing on mineral oil and reported that on thermal ageing the dielectric properties of oil reduces drastically [24]. Coulibaly *et al.* [25] have compared physicochemical properties of mineral oil and ester liquid on thermal ageing and have indicated the blanketing effect of N_2 in case of both the oils. Peppas *et al.* have observed the pre-breakdown phenomena in ester liquid and have established the efficiency of electrical measurements by mirroring the results in optical measurements [26].

With the increase in non-linear loads in power system network, the sinusoid gets distorted containing different harmonics with varying amount of THDs. Recently, it is observed that the THD of the supply voltage waveform has increased to more than 40% [27]. Han *et al.* have observed that the partial discharge inception voltage of polyamide film insulation remains constant with frequency variation [28]. Fig. 3 shows variation in CIV of thermally aged ester liquid under harmonic AC voltages with different THDs.

Not much variation in CIV is observed with increase in supply voltage frequency. This indicates that for corona discharges to take place in needle–plane electrode, the magnitude of supply voltage plays more important role than applied frequency. It is observed that increase in THDs shows a reduction in CIV (Fig. 3). Also, it is noted that irrespective of ambience in which thermal ageing of ester liquid is carried out, the CIV of aged liquid is less than that of the virgin liquid. Drastic reduction in CIV is observed with liquid aged in air ambience followed by He and N_2 ambiences.

By comparing the values of CIV, it is observed that harmonics of higher frequency have more impact on the CIV. Also, an increase in THD reduces the CIV. The cause for it could be due to the peak factor of the harmonics introduced. As the dv/dt of the supply voltage is more for higher-order harmonics of higher values, the inception is observed to occur at lower voltages. The result of the study indicates that the level of ageing of liquid is minimum when ageing is carried out in the N_2 medium.

The typical UHF signal measured due to corona activity in ester liquid is shown in Fig. 4(i). The fast Fourier transform (FFT) analysis of UHF signals due to corona activity in thermally aged liquid is shown in Fig. 4(ii). It is observed that the ageing has a negligible effect on dominant frequency (:1 GHz) of CIV waveform.

3.2 PRPD analysis

To understand the number of discharges and phase at which discharges occurs at different percentages of THD at different frequencies for the ester liquid samples and compare the effect of ambience, PRPD analysis was carried out [29]. Florkowski *et al.* have studied the partial discharges in insulation systems under harmonic voltage using PRPD technique and have concluded that the partial discharges resulting from distorted voltage cause the acceleration of ageing processes in the insulation systems. The presence of harmonics with increased THD affects the crest factor of the supply voltage waveform and the rate of rise of voltage have high impact on the insulation structure with increased partial discharge activity, thereby enhancing the degradation of insulation structure [30]. PRPD analysis is carried out with the help of spectrum analyser kept in zero span mode. The centre frequency is set equal to the dominant frequency of analysed UHF signal [Fig. 2(ii)]. To coordinate the peaks of spectrum analyser with the supply waveform, the oscilloscope, spectrum analyser and function generator are kept in sync mode. Signals are then given in burst mode (25 cycles) overlapping the harmonics at zero phase of sine wave. PRPD analysis of corona activity in ester liquid under AC and harmonic AC voltage with different THDs is shown in Fig. 5.

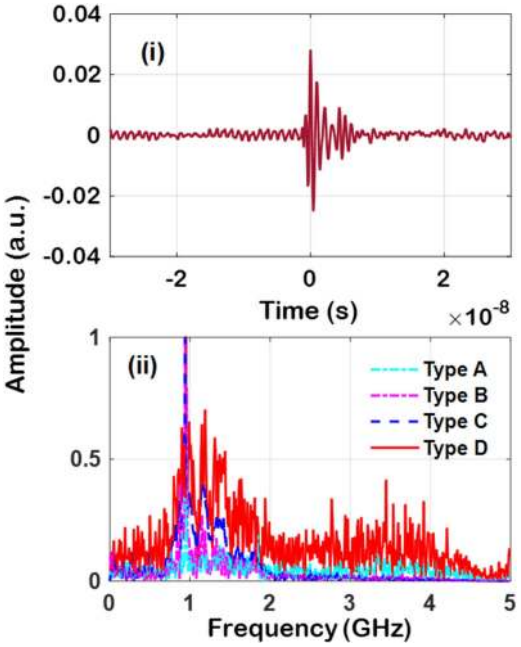

Fig. 4 *(i) Typical UHF signal formed due to corona activity in thermally aged ester liquid, (ii) FFT analysis of UHF signal formed due to corona discharge activity in different liquid samples*

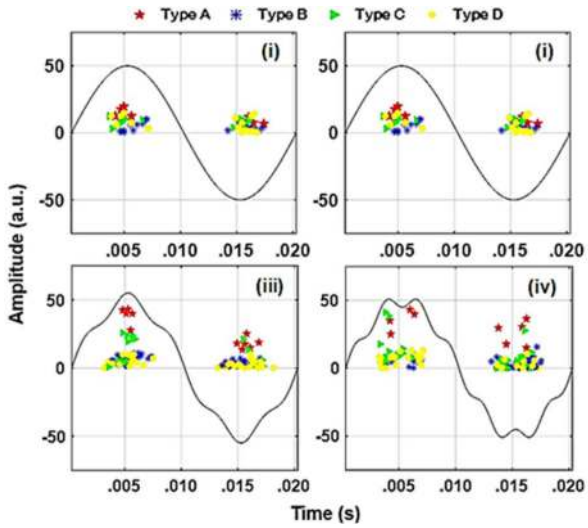

Fig. 5 *PRPD for sample types A, B, C and D for (i) fundamental frequency, (ii) 3f with 4% THD, (iii) 5f 10% and (iv) 7f with 10% THD*

Corona discharges are observed to occur at the peak of the waveform for different THDs. As the harmonic content increases, the number of discharges increases. It is observed that ageing in different ambiences results in significant variation in PRPD patterns. As indicated in Fig. 5, the virgin liquid has the highest discharge peaks compared with aged liquid in all the cases, which is similar to results obtained for mineral liquid ageing study [31].

This increase is more significant in the case of Type C compared with Type B. Also, it is seen that dispersion of discharges is more in liquid Type C. This indicates that the ageing of liquid is prevented more in the N_2 atmosphere. The decrease in the magnitude of discharges can be explained as a result of a decrease in CIV, which is observed for the aged specimen. It is observed that on ageing the number of discharges increases.

3.3 Physical changes in thermally aged ester liquid

Thermal ageing of ester liquid in different ambiences showed slight variation (intensification) in colour and gradual loss of transparency. Hamdi *et al.* observed characteristic variation in colour of the mineral oil on thermal ageing and have observed that

Table 1 Cut-off wavelength and CIE data of ester liquid under N_2, He and air atmosphere are shown at absorbance value of 0.5

Liquid samples	λ_{max} at $A = 0.5$, nm	CIE X	CIE Y
virgin ester liquid	330	0.19	0.15
N_2 day 7	345	0.16	0.12
N_2 day 14	348	0.16	0.12
N_2 day 21	350	0.16	0.12
He day 7	369	0.16	0.11
He day 14	376	0.16	0.09
He 21	377	0.16	0.07
air day 7	375	0.16	0.08
air day 14	396	0.16	0.07
air day 21	419	0.19	0.15

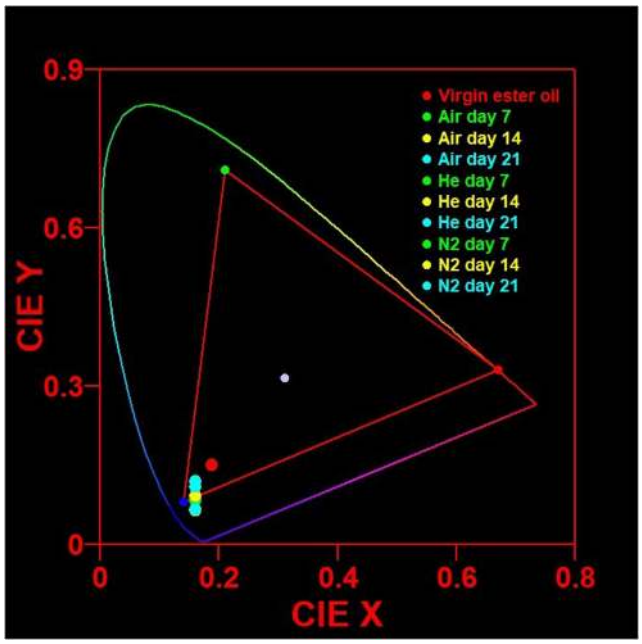

Fig. 6 *CIE X and Y colour indexes of ester liquid aged under different conditions as on 7th, 14th and 21st day of ageing (best viewed in colour online)*

the change is less when mixture of mineral oil ester liquid is used. A similar observation is made in the present paper, where drastic change in colour of the liquid is not observed, which is validated through Commission Internationale de l'Eclairage (CIE) values [3]. Although there is an intensification of colour with ageing, the colour coordinates do not appear to change as the spectral profile in visible range remains the same (as indicated by CIE [32]). The change in colour intensity is faithfully captured by light absorbance (UV–Vis spectrum). The absorbance data in the wavelength range 350–500 nm are selected to obtain CIE coordinates (i.e. CIE X and CIE Y) and depicted in Table 1 (and Fig. 6). CIE values are meant to be obtained in visible region of spectrum (350–800 nm) and ester liquid variants absorb strongly in the UV region of spectrum (Fig. 7). Consequently, the changes observed in CIE X and CIE Y values of E oil variants are minimal over the ageing period. Ester liquid in N_2 environment shows the least change in colour due to ageing. The intense colouration of ester liquid in the air medium appears due to rapid oxidative degradation and pigmentation. During thermal degradation, molecular level changes take place in oil; homolytic cleavage of carbon–carbon or carbon–hydrogen bond takes place. Smaller free radicals (such as hydrogen, methyl and ethyl) are relatively stable; larger free radicals breakdown to form smaller, more stable radicals and other unsaturated olefin compounds. The free radicals are reactive and they undergo chain reactions to form lighter lower boiling unsaturated compounds, gases and additional free radicals [21].

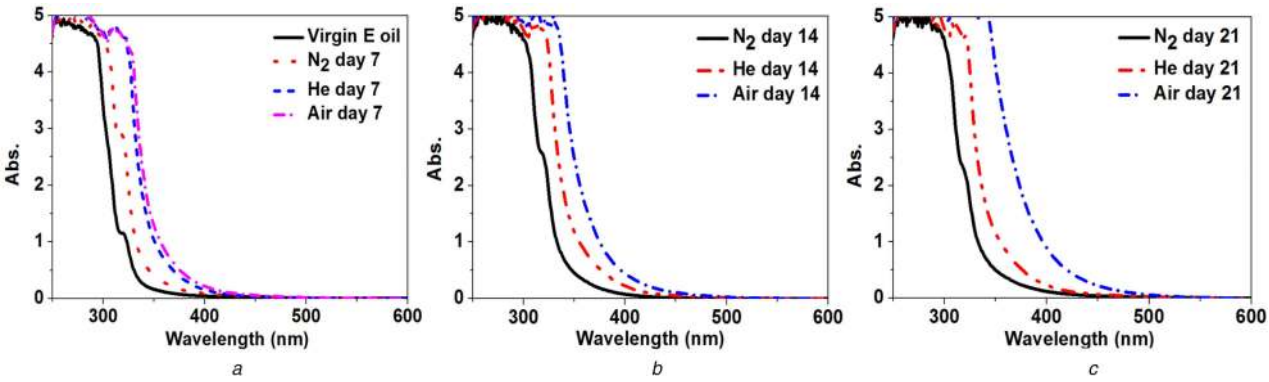

Fig. 7 *UV–Vis absorption spectra of ester liquid under N_2, He and air medium as on*
(*a*) Day 7, **(*b*)** Day 14, **(*c*)** Day 21

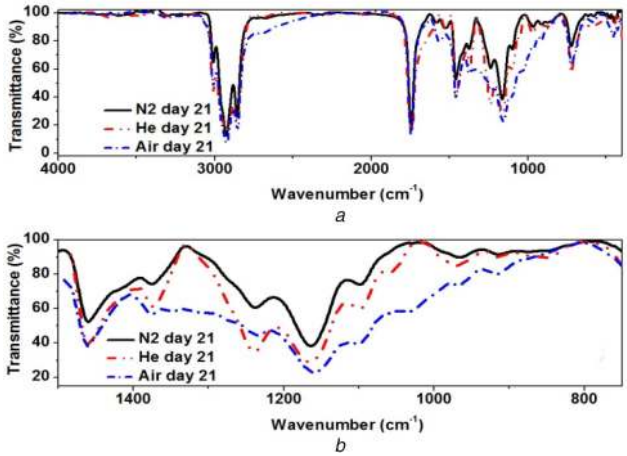

Fig. 8 *IR spectra of ester liquid on the 21st day under N_2, He and air medium of ageing*
(*a*) From 400 to 4000 cm^{-1}, **(*b*)** From 700 to 1500 cm^{-1}

The ageing of ester liquid depends on processes such as hydrolysis and oxidation. Hydrolysis results in increased acidity in liquid matrix. The increase in viscosity of the liquid is due to oxidation and it is directly proportional to temperature [33]. Variation in viscosity of the ester liquid due to thermal ageing at different ageing condition was measured during the ageing process on days 7, 14 and 21. Viscosity was directly measured without any pre-treatment of liquid samples. Table 2 shows the viscosity data of ester liquid variants at two different temperatures (25 and 30°C). As expected, the viscosity values of liquid samples at higher temperature are less than that at a lower temperature.

Furthermore, for any particular day, thermally aged ester liquid in air medium is more viscous than that under He or N_2 medium. The viscosity of ester liquid under He and N_2 medium shows comparable viscosity values with not much of difference. The cause for variation in viscosity of ester liquid during thermal ageing in different ambiences is due to the level of degradation of ester liquid. The higher viscosity in air medium is due to the formation of oxidative breakdown products; further heating causes those moieties to agglomerate, resulting in enhanced viscosity. Owing to higher density of N_2 compared with He rich ambience will restrict the oxygen interaction with the oil during thermal ageing. In the process, the level of degradation is minimum and the characteristic changes in properties of ester liquid are observed including viscosity.

3.4 IR spectrum

Fig. 8 shows the FTIR spectrum of thermally aged ester liquid in the air, N_2 and He medium as on day 21. Considerable change has not appeared in the IR profile of the liquid samples under different heating conditions. We could observe minimum variation in the fingerprint region (700–1400 cm^{-1}) of the spectrum. The variation occurring in fingerprint region of the spectrum is difficult to describe since its overlapped region of C–C, C–O, C–N, C = C and C = N stretching frequencies. Ray *et al.* [34] have shown the presence of broad fingerprint region in the IR spectra of fluorescent carbon nanoparticles. They identified the peaks in this region could be due to C–OH, C = C, C–O–C and C-H stretching frequencies. In the present paper, with ageing, the absorbance around the fingerprint region increases in air medium; this could be due to the formation of polar C–O bonds as a result of oxidation. During the ageing process, due to high temperature and absorption of oxygen and water, oil undergoes a number of chemical reactions such as hydrolysis, oxidation, isomerisation and polymerisation [18]. When ageing is carried out in air medium, the oxidation becomes rapid; as a result of which, new molecular moieties containing C–O–C are formed in oil matrix. The stretching frequency of C–O bond lies in the fingerprint region of the IR spectrum.

Generally, mineral oil generates carbonyl containing species such as aldehyde, ketones and esters with ageing, consequently, a peak at around 1600 cm^{-1} is produced with ageing. However, ester liquid did not show any such developments.

Table 2 Viscosity of thermally stressed ester liquid under N_2, He and air atmosphere at two different temperatures

	Viscosity, mPa s	
	25°C	30°C
virgin ester liquid	57.8	47.9
N_2 day 7	58.1	48.8
N_2 day 14	61.1	50.8
N_2 day 21	62	51
He day 7	61.1	50.8
He day 14	62.9	52.2
He day 21	63.2	52.6
air day 7	61.3	50.5
air day 14	70.3	58.2
air day 21	75.3	62.2

3.5 UV–Vis spectrum

Fig. 7 shows the UV–Vis absorption spectra of ester liquid under different conditions of heating as on 7th, 14th and 21st days. It is observed that with ageing, the leading edge of absorption band shifts toward the red region of the spectrum. This is due to oxidation of ester liquid in the presence of oxygen, moisture and thermal stress. As a consequence of oxidation, new chromophoric moieties are formed. The newly formed chromophoric moieties start absorbing strongly in the UV–Vis region of the spectrum and hence there appears a progressive red shift of the absorption band. It can also be understood as with ageing the concentration of liquid increases.

Table 1 shows the cut-off wavelength for absorbance value of 0.5. For any particular day, liquid sample with exposure to air shows the highest absorbance than liquid in He and N_2 mediums.

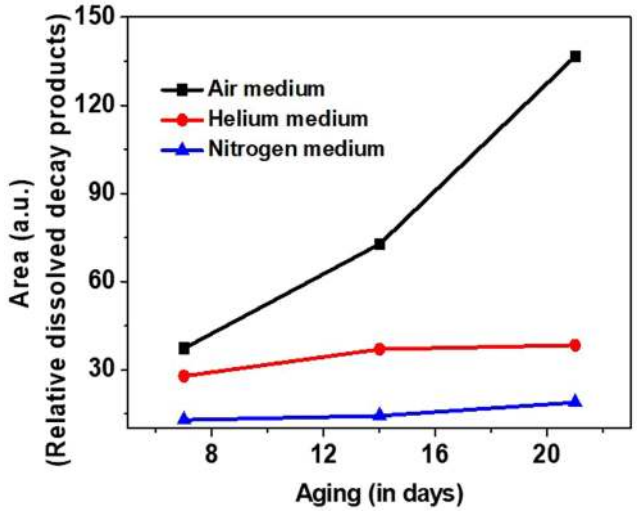

Fig. 9 *Relative DDP with ageing time under different ambiences*

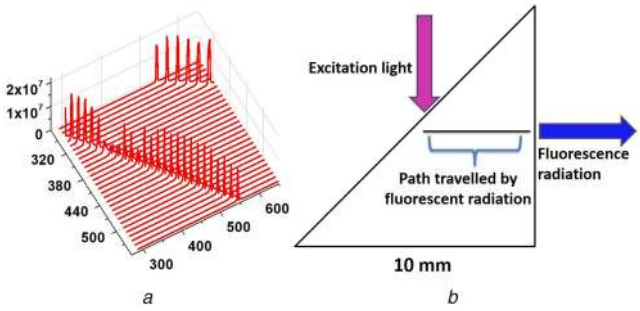

Fig. 10 *Fluorescence measurement with different cuvette orientations*
(a) Front face EEM spectra of thermally aged ester liquid showing only Rayleigh scattering and no fluorescence; ***(b)*** Schematic diagram of cuvette orientation for back-face fluorescence measurement

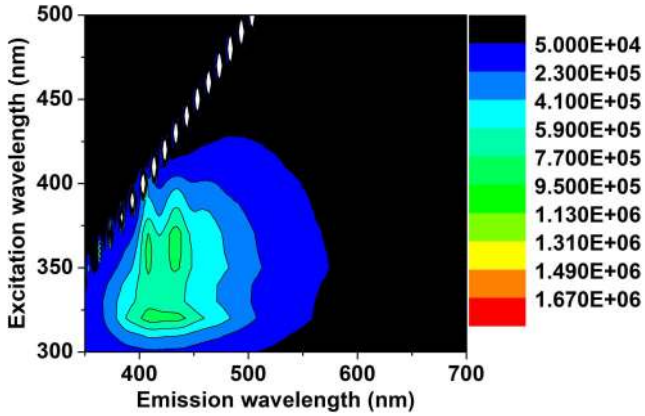

Fig. 11 *EEM fluorescence of virgin ester liquid*

The presence of inert atmosphere significantly decreases the formation of chromophoric moieties and results in reduced rate of ageing compared with air medium. Furthermore, under N_2 medium, the ageing is slower than that under He medium. This can be explained by the relative content of dissolved decay product (DDP) in different ester liquid variants evaluated from the absorbance curves in the visible range (350–600 nm for this paper) [35]. The results are summarised in the following Fig. 9. It is observed that the relative DDP formation is highest when oil is aged in air medium and is the lowest when oil is aged under N_2 purging condition.

3.6 Fluorescence spectrum

As ester liquid is a multi-component system, the fluorescence spectral properties can be better understood through the 3D EEM profiles of the liquid samples. To avoid inner filter effect and scattering from liquid matrix, a triangular cuvette is used for measurement of all fluorescence spectra. Front face fluorescence detection is an established technique for measuring fluorescence of optically dense and scattering systems. However, since ester liquid is a viscous liquid and its fluorescence is weak, the front face mode of fluorescence observation is not quite successful. It is observed that in front face geometry, the scattering from the sample and cuvette surface always dominated fluorescence signature of ester liquid.

EEM spectrum of ester liquid recorded in front face mode shows only first- and second-order Rayleigh scattering (Fig. 10*a*) and no fluorescence from ester liquid is observed. Contrary to this when we used back-face observation of EEM spectrum (Fig. 10*b*), the scattering radiation is significantly reduced and fluorescence signature shows up quite prominently. Unlike front face measurement, the back-face fluorescence data acquisition ensures (i) enhanced fluorescence signature of the analyte, (ii) excludes the second-order scattering and (iii) the intensity of Rayleigh scattering is minimised. The superiority of such a method is clearly visible in the contour EEM landscape of Figs. 11 and 12. Fig. 11 shows EEM spectra of virgin ester liquid. Fig. 12 shows the EEM spectra of other liquid variants on 21st day.

Each EEM spectrum has a maximum at a particular emission wavelength for a corresponding excitation wavelength. Table 3 depicts the fluorescence emission maxima of all the ester liquid variants in terms of excitation–emission wavelength and the intensity values. Fig. 13 shows the fluorescence spectra of ester liquid variants as on 7th, 14th and 21st days at a particular excitation wavelength (excitation wavelength is 320 nm). It is observed that initially there is an increase in fluorescence intensity at around day 7 of heating compared with virgin ester liquid (Fig. 13*a*). Owing to thermal stress and in the presence of oxygen as well as moisture, ester liquid gets oxidised and new chromophoric molecular species are formed. The newly formed moieties are fluorescent in nature and hence the fluorescence intensity of ester liquid increases at around 7th day of ageing. Further heating results in a gradual decrease in fluorescence intensity and there appears progressive red shift in emission maxima of liquid samples. With ageing, the concentration of chromophoric moieties in liquid matrix increases and they accumulate gradually to form larger carbonaceous particles. Hence the loss of fluorescence intensity is due to concentration-dependent quenching [36].

From Fig. 12, Table 3 and Fig. 13, it is evident that the redshift and loss of intensity are more pronounced in air medium compared with inert gas medium. When ester liquid is in air medium, it shows a greater degree of redshift both in terms of excitation and emission spectra (Fig. 12). The presence of air considerably fastens the ageing of ester liquid. For a particular day, emission intensity obtained in N_2 medium is the maximum; this suggests that under N_2, rate of oxidative degradation is least experienced. N_2 gas effectively dislodges oxygen from the liquid matrix, and thereby reduces the oxidative degradation of liquid. He also shows reduced ageing than air; however, the low molecular mass of He is not as suitable as N_2 toward removing oxygen from liquid matrix.

4 Conclusion

Important conclusions accrued based on the present paper are the following:

- CIV under AC and DC voltages of thermally aged ester liquid reduces irrespective of ageing ambience. The decrease is maximum with thermally aged liquid in air medium followed with He and N_2 ambiences. The CIV is high under negative DC compared with positive DC and AC voltages.
- The CIV with thermally aged ester liquid under high-frequency AC voltages is nearly the same. A significant reduction in CIV is observed under harmonic AC voltages with higher THDs.
- The UHF signal formed during corona discharge activity has a dominant frequency at near 1 GHz.

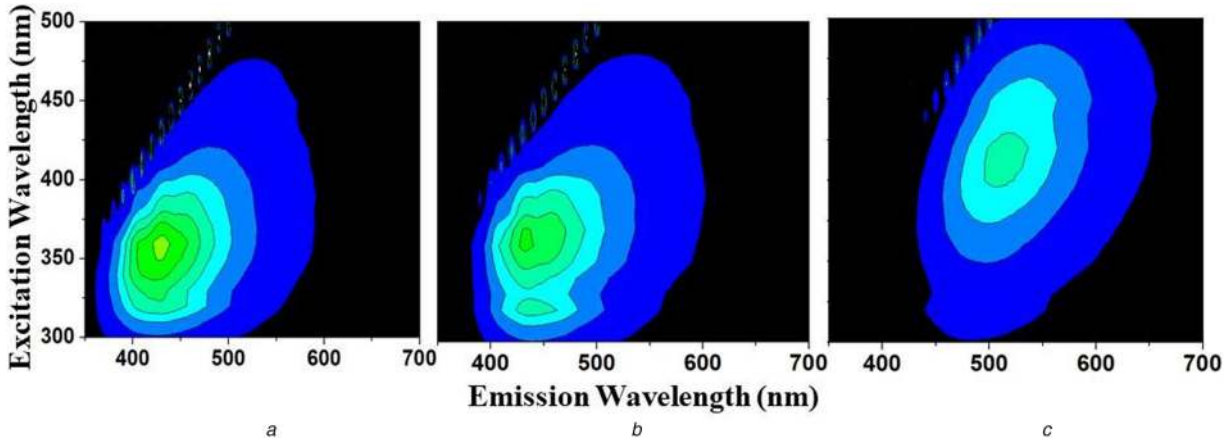

Fig. 12 *EEM spectra of ester liquid on 21st day*

(a), ***(b)***, ***(c)*** represent Contour plots of EEM spectra of ester liquid in N_2, He and air mediums as on 21st day of ageing respectively (Intensity labels are same as Fig. 11)

Table 3 Emission maxima at 320 nm excitation (column 2); EEMF data depicts maximum ex/em and corresponding intensity (columns 3–5)

Ester liquid variant	Ex at 320 nm Em. maxima	EEMF data λ_{ex} max	λ_{em} max	Intensity
virgin ester liquid	412	320	412	8.71×10^5
N_2 day 7	430	360	428	1.37×10^6
N_2 day 14	432	360	430	1.39×10^6
N_2 day 21	434	360	430	1.21×10^6
He day 7	438	320	440	9.03×10^5
He day 14	439	370	432	1.66×10^6
He day 21	439	370	434	9.73×10^5
air day 7	442	370	432	1.31×10^6
air day 14	462	390	480	5.46×10^5
air day 21	484	410	512	6.46×10^5

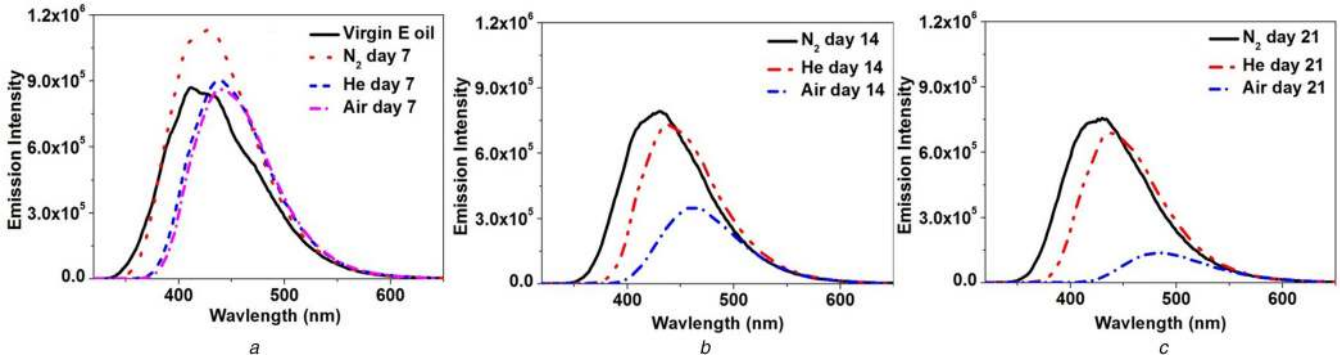

Fig. 13 *Fluorescence emission of ester liquid under N_2, He and air medium as on*

(a) Day 7, ***(b)*** Day 14, ***(c)*** Day 21; excitation wavelength is 320 nm

- PRPD analysis indicates that the magnitude of discharges is low and the number of discharges is high with thermally aged ester liquid.
- FTIR analysis of thermally aged ester liquid indicates the formation of carbonaceous particle due to thermal ageing. UV analysis of thermally aged ester liquid shows characteristic variation in the UV–Vis region of the spectrum.
- N_2 gas effectively dislodges oxygen from the liquid matrix, and thereby reduces the oxidative degradation of liquid. He gas also shows reduced ageing than air; however, the low molecular mass of He is not as suitable when compared with N_2 toward removing oxygen from liquid matrix.
- The loss of fluorescence intensity and redshift in fluorescence maxima is the fingerprint to indicate characteristic variation of ester liquid due to thermal ageing.

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