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Investigation of Transformer Oil Aging Under Service Load from Various Dielectric Measurements, Chemical Analysis and Spectroscopy

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ABSTRACT. This work presents the experimental results of the effect of field strength and temperature on the dielectric and physical properties of transformer oil sampled from EHV transformer operating for the past seven years. Aged oil was compared with fresh transformer oil and the impact of filtration and degassing on the dielectric, and physical properties are discussed. Viscosity, relative humidity and cations content are correlated with dielectric properties. Experimental studies reveal that dielectric loss index for all samples is field independent but temperature dependent and increases exponentially as the temperature is increased. Dielectric loss index provides a reliable picture of oil aging as its value increases rapidly with the age of oil. Ferric iron content is increased by large factor due to aging. Carbonyl groups and polar products could not be detected in the oil samples using GC, IR, PMR and ^{13}C-NMR techniques of spectroscopy.

Aged transformer oil exhibits complex and interdependent physical, chemical and electrical properties. Many processes and variables are involved and their interaction is not fully explained. A suitable test to gauge the condition and health of the oil during the service which could be technically viable and economical is not yet characterized. Research field has been intensively developed after the second world war (years 1950-1970) (CIGRE-Committee 15, on 'insulating oils' and committee 12 on transformers); Annual report of the conference on Electrical insulation and dielectric phenomena-National Academy of Sciences U.S.A.; Symposium on insulating oil - Annual Meeting of ASTM). Recently a number of authors have suggested different techniques and properties to evaluate the transformer oil aging (El-Sulaiman *et al.* 1982, Crine *et al.* 1982, Dudokovic *et al.* 1978 and Egger *et al.* 1981). It was claimed (El-Sulaiman *et al.* 1982) that the conduction current and acidity are related to the oil aging; moreover, spectroscopy

did not indicate significant difference in five years aged oil. Others have reported (Crine *et al.* 1982) that the dielectric loss and breakdown do not provide a reliable picture of the degree of oil aging. It was recommended to use a combination of interfacial tension, antioxidant and HPLC analysis as useful clues. On the other hand the dielectric loss index was shown to be important in highly stressed transformer as it was shown that the change with aging may be much more significant (ASTM-Standard Test Method).

Modified methods of IEC-74 for measuring dielectric dissipation factor, specific electrical resistance, and IEC-474 for the measurement of the sludge and acidity have been described but they were claimed to have positive and negative aspects (Dudokovic *et al.* 1978). The insulation condition of aged transformers had also been studied by measuring breakdown voltage, dissipation factor, interfacial tension, neutralization value, saponification number and Warmann's value of their oils. It has been stated that measure of the values rises with the increase of oil age. Also, all measured characteristics were largely independent of the size of the transformer and the extent of the load (Egger *et al.* 1981).

This paper attempts to investigate the properties of service aged oil by measuring its dielectric loss index, viscosity, relative humidity and cations analysis. Moreover, changes occuring in the chemical structure of oil are also studied by employing GC, IR, PMR and ^{13}C-NMR techniques of spectroscopy. Results are compared with the similarly treated fresh oil which conformed to BS: 148-1972, and some interesting values for understanding the problem of aging are discussed.

Experimental

(A) Eectrical

Aged oil is sampled from an outdoor 100 MVA; 115/66 kV transformer, fitted with Silica gel breather and oil conservator, with a maximum oil temperature rise of 55°C. This unit has been operating for the last seven years without any fault and replacement of oil. This unit is installed in a refinery located in the desert, but not far from the sea coast, where ambient temperatures vary from 0 to 47°C and relative humidity ranges from 60 to 70%.

The filtered (F4) oil test samples are first dehydrated by passing through a one meter long chromatographic column containing non-adsorbent silica gel and then passed through a sintered glass filter of pore size 5-15 μm. Degassed oil samples are prepared by heating the oil (as received) for 30 minutes at 220°C.

The electric properties such as capacitance and dissipation factor were measured according to ASTM D924-76 using Tettex high voltage precision capacitance bridge type 2821 at 60 Hz and the measuring accuracy was better than ± 1%. The schematic diagram for the experimental set up is shown in Fig. (1). Measurements were made under a field varying from 1.5 to 9.5 kV cm^{-1} and

temperature were varied from 27°C to 140°C under a vacuum of 1.0 Pa, using Edwards rotary vacuum pump type ES100. A three terminal liquid test cell, Tettex type 2903 conforming to VDE 0370 was used as sample holder. The cell constant was determined by calibration with specially purified benzene. A cell constant correction factor for temperature variations was also accurately determined for the temperature range covered in the measurements. Sample temperature was adjusted by using Tettex control unit type 2966. Temperature uniformity and constancy were within ± 1°C during the measurement period.

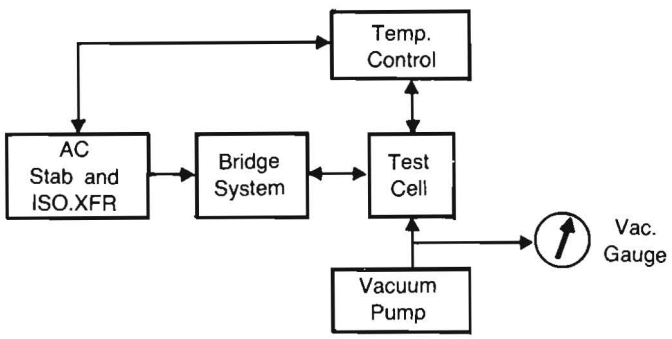


Fig. 1. Experimental set-up.

The cell was filled with a 40 ml sample of oil taking care that no bubbles occurred. The cell electrodes were cleaned by thoroughly washing them three times with distilled benzene and afterwards dried at 110°C for a period of half an hour. The cell was completely dismantled and cleaning procedure was repeated after each set of measurements.

In order to avoid the time dependence of tan δ, all the measurements were carried out within one minute after the application of electrical stress.

(B) Physical

The dynamic viscosity of different oil samples was measured using a Brook-field viscometer model LVT at varying temperature from 24 to 80°C and shear rate varying from 0.73 to 73.42 s^{-1}.

The relative humidity of the oil samples was measured using a Foster dryness test set at temperature range varying from 18 to 60°C.

(C) Chemical and Spectroscopic Analysis

Four oil samples were selected, namely fresh as such (FA), fresh-degassed (FD), aged as such (AA) and aged-degassed (AD) and were subjected to the following determination:

The oil sample (10 g) was dissolved in chloroform (10 ml) and then extracted with ultra pure 20% HNO_3 acid (100 ml) five times using 20 ml portions of 20% HNO_3 and the acidic extract was then subjected to cations determination for Fe^{+++}, Cu^{++} and Pb^{++} using AA75 atomic absorption spectrometer.

The IR spectra of the oil samples were recorded as films on a Parkin-Elmer 580B infrared spectrometer. These were scanned from 625 cm^{-1} to 4000 cm^{-1}.

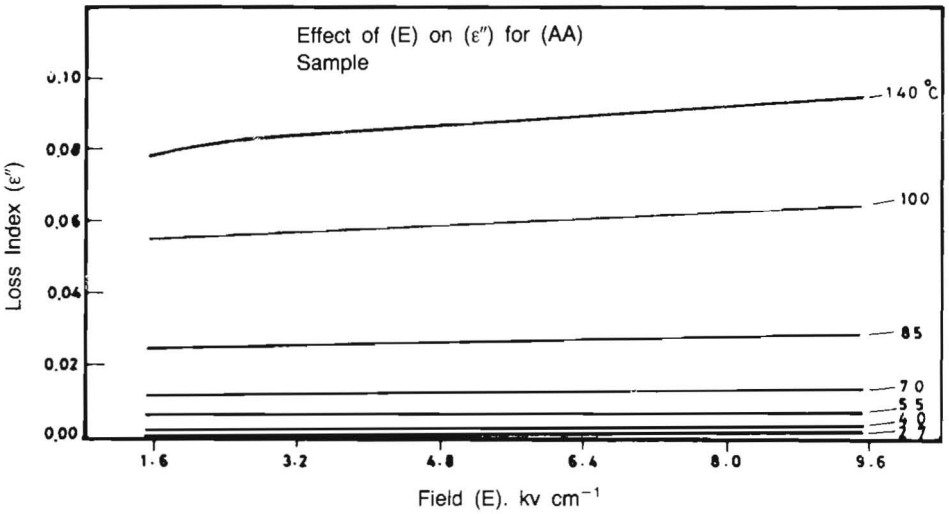
The PMR spectra of the oil samples were recorded in carbon tetrachloride using tetramethylsilane (TMS) as an internal standard on a Varian T60A-60 MHz NMR spectrometer.

The ^{13}C-NMR spectra of the oil samples (noise-decoupled and off-resonance) were recorded in deutrated chloroform ($CDCl_3$) using tetramethylsilane as an internal reference on a Varian FT-80-80 MHz instrument. The samples were measured at 22°C and using 10 mm sample tube. The data consist of 8192 data points (DP) over 4000 Hz spectra width.

The GC spectra for the oil samples were obtained on a Varian 3700 GC instrument under the following conditions: *(a)* column: 30% OV-1 on Gas chrom. Q 100 # at 200°C, injector temperature 200°C. *(b)* Temperature programming: 200°C for 3 min. then increased to 250°C and 6°C/min. (c) Carrier gas: Helium at 10 ml/min. *(d)* Detector: Flame ionization detector (FID) at 300°C. *(e)* Chart speed: 1.0 cm/min. standard sample of C_{12} to C_{22} paraffin was used.

Results and Discussion

The values of dielectric loss index ε'', were derived from the measured values of dissipation factor tan δ, and capacitance for aged oil taken as such (AA), fresh oil as such (FA) and fresh oil filtered (FF4). Fig. (2) indicates these results at different fixed temperatures and it can be stated that ε'' is a weak function of field strength within the shown range for (AA) and (FA) (Fig. 2a and b, respectively). Other oil samples exhibit similar phenomenon. Fig. (3) is an example of the trend of deviation in tan δ/tan δ_O with field strength which reveals that the deviation at lower temperature is pronounced while it becomes very small at temperatures higher than 55°C, whereas the $\varepsilon'/\varepsilon_o$ is constant with the variation of field strength at all temperatures. The variation of dielectric loss index ε'', with field strength are summarized in Fig. (4) to compare the performance of different oil samples at 70°C, bearing in mind that all the samples exhibit similar behavior between a temperature of 27°C to 140°C. It can be seen from the curves of oil samples (AA) and (FA) that the dielectric loss index is increased considerably with the aging of the oil. The same result holds good even if the oil is filtered, as is clear from the curves for oil samples (AF4) and (FF4). This could be attributed to the increase in oil conductivity due to aging (El-Sulaiman *et al.* 1982).



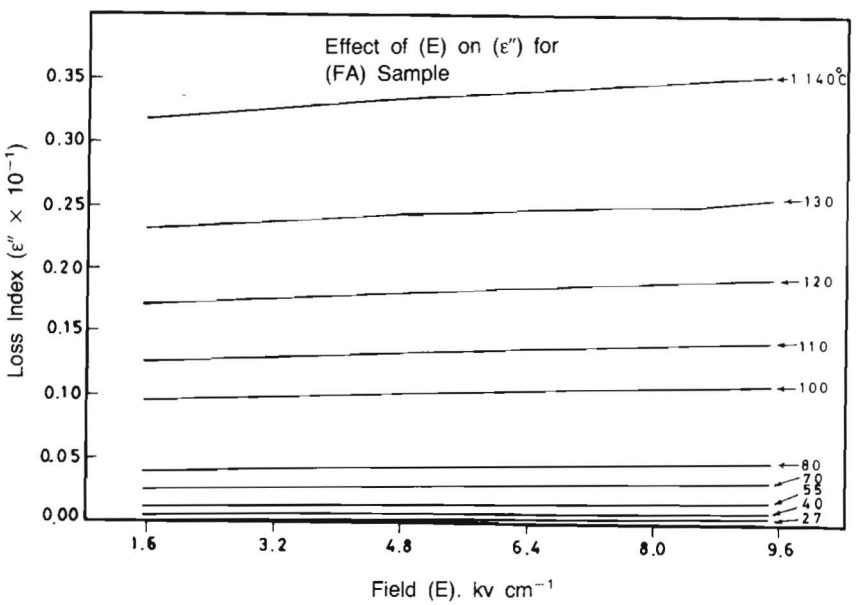


Fig. 2. Effect of field strength E on dielectric loss index ε″ for (a) aged oil as such (AA) and (b) fresh oil as such (FA).

Degassing the oil samples increases ε″, by a large factor as compared to fresh and aged oil as such and filtered oil samples.

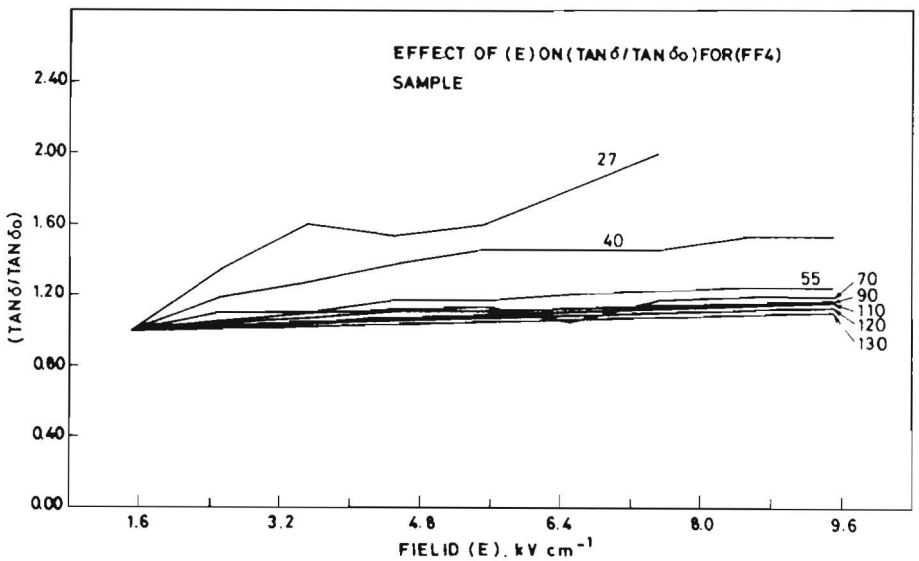


Fig. 3. Effect of field strength E on tan δ/tan δ_o for filtered fresh oil (FF4).

Interesting phenomena occur in aged degassed (AF4D) and fresh degassed (FF4D) oils. The dielectric loss is considerably increased in fresh oil as compared to aged oil. This is a clear index that profound chemical disintegration has taken place in aged oil as compared to fresh oil in such a way that aged degassed oil conducts less current than the fresh degassed oil. It is interesting to notice that the filtration increses ε″ in both aged and fresh oils. This could be attributed possibly to the decrease of the viscosity or increase in the relative fluidity (El-Sulaiman *et al.* 1982). Since it has been claimed before (Musil *et al.* 1982) that the breakdown strength of insulating oil is actually a function of relative humidity rather than the absolute moisture content in ppm, it was decided to investigate the effect of relative humidity on physical and dielectric properties. Fig. (5) explains the behaviour of different oil samples with respect to the relative humidity. It can be deduced from these curves that the effect of aging and filtration on relative humidity in a temperature range of 20° to 60° is represented by the following inequalities:

$$AA > FA > AF4 > FF4 \qquad (1)$$

This indicates that the relative humidity in aged oil is greater than the fresh oil.

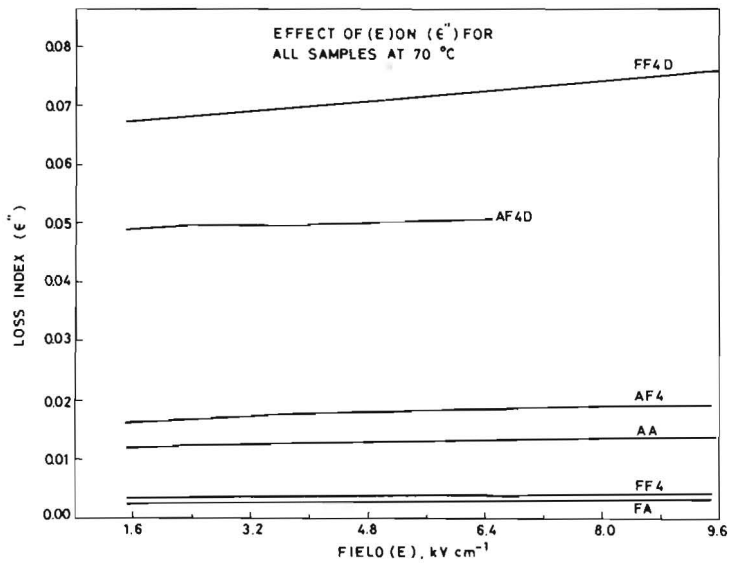


Fig. 4. Effect of field strength E on dielectric loss index ε″ for all oil samples at 70°C.

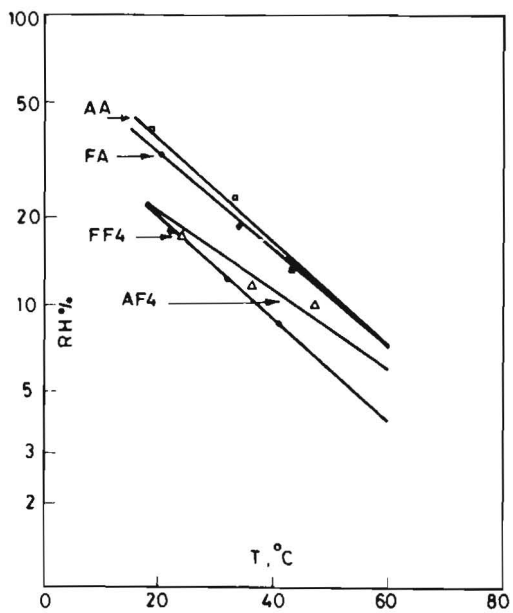


Fig. 5. Effect of relative humidity vs temperature for oil samples.

Refining by filtration reduces the relative humidity considerably in both oil samples.

Fig. (6) displays the variation in dynamic viscosity as a function of temperature in the range of 20 to 90°C on semi-log plot for different oil samples.

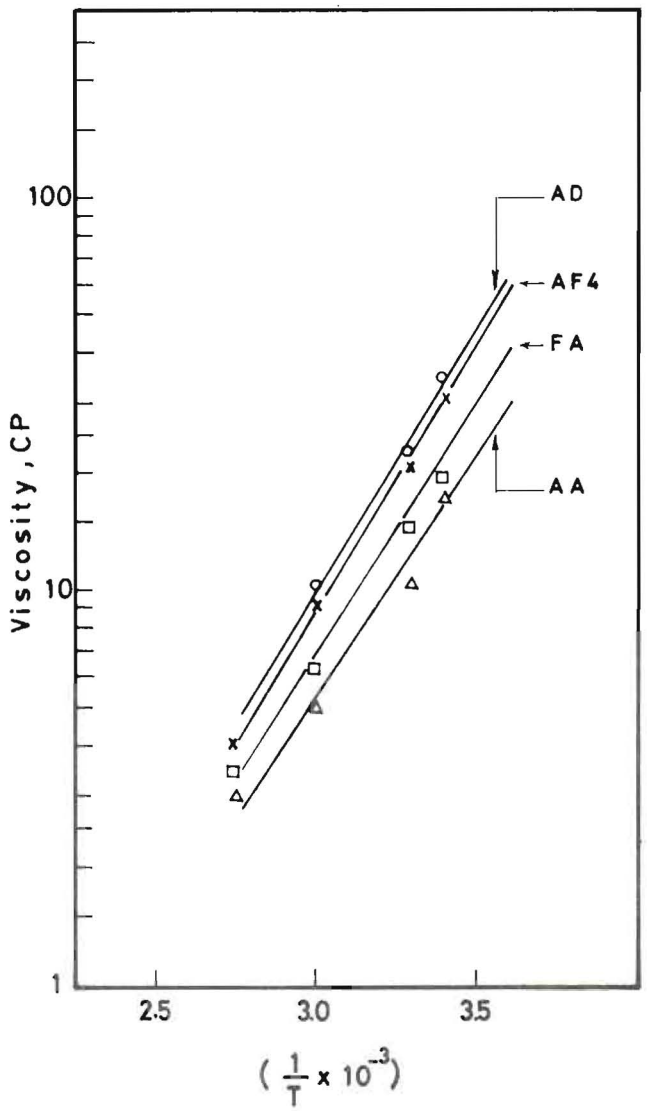


Fig. 6. Viscosity vs temperature.

Generally, the relationship between viscosity η, and temperature T, can be expressed as $\eta \propto EXP(-n/T)$ where n is a constant for all oil samples. It can be seen from these curves that the effect of aging, filtration and degassing on the oil viscosity is represented by the following inequality:

$$AD > AF4 > FA > AA \quad \ldots \quad (2)$$

which interprets that the viscosity of aged oil is lower than the fresh one and that is possibly because of the temperature rise and oil contamination during the service. This fact is proved when the aged oil is filtered and as a result its viscosity is increased which implies that pollution in the oil tends to decrease the viscosity. Degassing of aged oil suggests pronounced increase in viscosity which possibly has resulted due to chemical interaction. Moreover, it is clear from Fig. (6) that the apparent dynamic viscosity of the oil samples decreases with the increase in temperature and this value remains constant as the rate of shear is varied Fig. (7) indicating newtonian behavior.

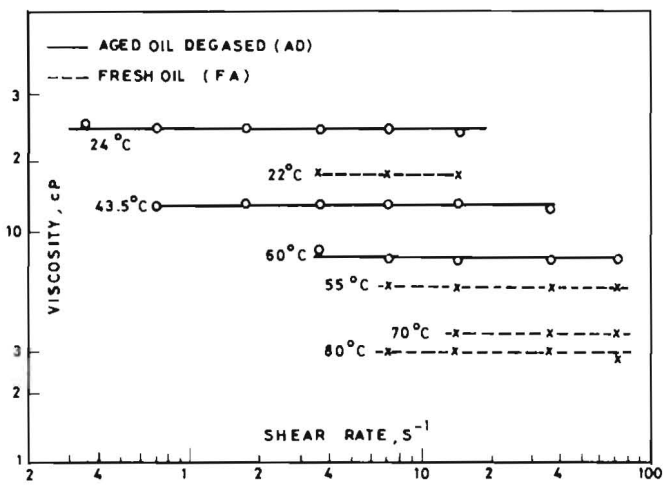


Fig. 7. Viscosity of transformer oil vs shear rate.

It is interesting to deduce from the inequalities (1) and (2) that there exists a correlation between viscosity and relative humidity which may obey the proportionality $\eta \propto RH$. This proves that the relative humidity effects the viscosity which in turn is also varied, because of oil contamination. Thus measurement of viscosity is also one of the factors that can be used to evaluate the deterioration of the oil.

Dielectric properties as a function of temperature

The variation of dielectric loss index ε'', with temperature is plotted in Fig. (8) to compare the performance of different oil samples at fixed field strength of 2.5 kV cm^{-1}. It can be stated that ε'' is a strong function of temperature. The curves of oil samples (AA) and (FA) show that ε'' is increased appreciably with the aging of the oil. The same trend holds good even if the oil is filtered as clear from the curves of oil samples (AF4) and (FF4). These effects, aging and filtration, are similar to those already noticed in Fig. (4). This experimental evidence supports the hypothesis put forward by (El-Sulaiman *et al.* 1983) while working on filtration and burst current in aged oil stating that filtration of the oil using small pore size filter makes the oil more homogenized with lower density and high relative fludity. Similar results, have also been noticed by (Rabe *et al.* 1979) while working in silicon oils. The dielectric loss index increases markedly with the increase in temperature obeying exponential law $\varepsilon'' = EXP\ (mT)$ which reflect the charge carrier transfer through the potential barrier m, by the mechanism of thermic excitation. This is to say that the exponential term is in connection with frequency, with which, charge carriers go across the barrier. From Figure (8), the experimental activation enthalpy value of charge carriers (ions) responsible for

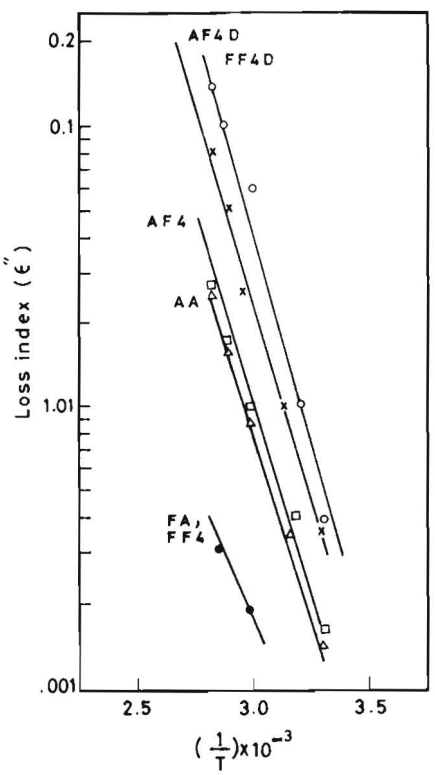


Fig. 8. Effect of temperature on dielectric loss index at 2.5 kV cm^{-1} for all oil samples.

power loss index can be found. The curves of degassed oils (AF4D) and (FF4D) again exhibit considerable increase in ε'' suggesting chemical interaction.

Chemical and Spectroscopic Analysis

It is evident from table (1) that the ferric iron content in the fresh oil samples was not detected where as it was 27.80 ppm and 24.40 ppm in aged oil as such and aged oil degassed respectively. The Cu^{++} and Pb^{++} cations for all the samples are very low and of the same magnitude. The high content of Fe^{+++} iron in aged oil may be due to easier leaching from the transformer as compared to Cu^{++} and Pb^{++}. Therefore its presence might contribute significantly in the deterioration of the insulating properties of the oil, while both Cu^{++} and Pb^{++} play non-significant role in this respect.

Table (1): Cations content of the oil samples (ppm)

Oil samples / Cations ppm	FA	FD	AA	AD
Fe^{+++}	Nil	Nil	27.80	24.40
Cu^{++}	0.60	0.45	0.60	0.60
Pb^{++}	1.20	1.35	1.95	1.20

Fig. (8) shows that the cruve of aged oil sample (AF4D) exhibits larger ε'' as compared to aged oil sample (AF4). This might be due to the presence of Fe^{+++} iron in bound form with the low molecular weight hydrocarbon content of the aged oil sample (AF4) which on degassing breaks to liberate free Fe^{+++} iron. This consequently results in an increase in conduction current (El-Sulaiman *et al.* 1982) and hence the dielectric loss index ε'' increases.

The IR spectra of the aged and fresh oil samples were identical in all respects. They showed the presence of open chain aliphatic and alicyclic (naphthenes) hydrocarbons. The technique was not able to detect the aromatic hydrocarbons which are usually added to the insulating oils as antioxidants. This is indicated by the absence of bands at 1500, 1580 and 1600 cm^{-1}. It also shows the absence of carbonyl compounds indicated by the absence of absorption bands at 1680–1750 cm^{-1} Fig. (9). This is in contradiction to the results of Crine *et al.* (1982) where they claimed the presence of carbonyl products by IR spectroscopy in the same range, but also speak of the inconsistency of their results. Polar products, such as those containing OH, CH, COOH, have not been detected in the range of 2500–3590 cm^{-1}.

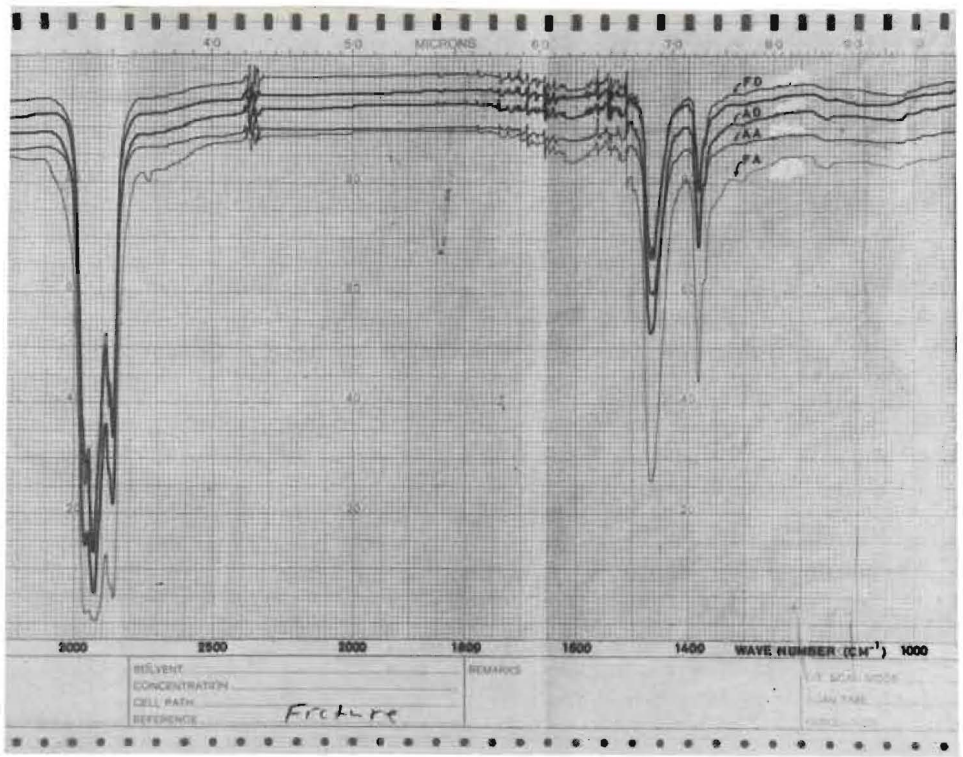


Fig. 9. IR-spectra for transformer oil samples.

The proton spectra of the oil samples in CCl_4 and TMS were identical displaying characteristic absorption bands as, (a) multiplet centered at 0.87 ppm and a singlet at 1.23 ppm indicating the presence of aliphatic open chain and alicyclic hydrocarbons, (b) quartet centered at 6.83 ppm indicating the presence of aromatic compounds added as antioxidants. However, there is no evidence for the presence of carbonyl compounds (CHO, CO, COOH).

The noise-decoupled ^{13}C-NMR spectra of the oil samples in deuterated chloroform were almost identical, displaying ^{13}C-signals with chemical shifts ranging from 10.94 to 39.58 ppm, (aliphatic open chain and alicyclic hydrocarbons) and from 125.52 to 129.11 (aromatic compounds). This again confirms the presence of aromatic compounds additives as antioxidants. The off-resonance spectra showing ^{13}C-proton coupling are also identical, displaying quarters and triplets for CH_3- and CH_2- carbon-proton coupling. The absence of the carbonyl compounds has been confirmed also through this techniques as indicated by the absence of carbon signals from 160 to 220 ppm.

The GC spectra of the fresh and aged oil samples are identical with very little difference, revealing the presence of the different components with retention time ranging from 1 to 3 min. It simply indicates the presence of C_{18} to C_{22} hydrocarbons, Fig. (10). These results acquired through different techniques of spectroscopy do not elucidate the oxidation products that have been formed in the aged oil which are otherwise existing as proved from electrical tests. This means more sophisticated techniques like HPLC should be tried.

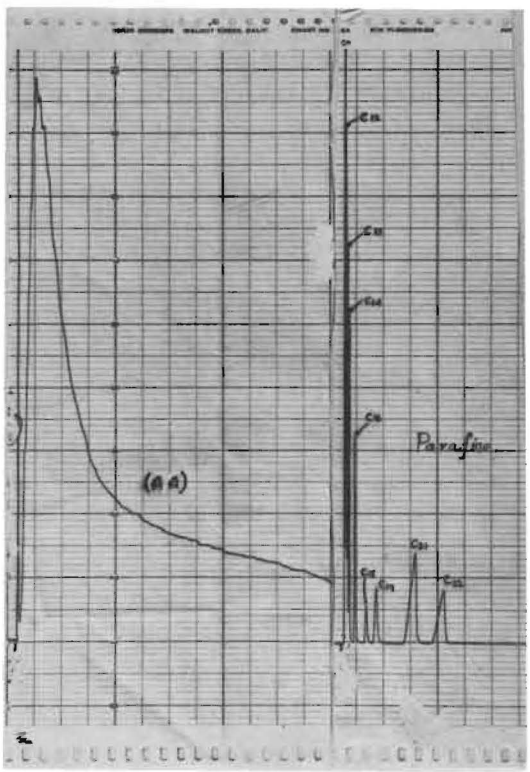


Fig. 10. Gas chromatograms of aged oil sample (AA) and standard paraffin.

Conclusions

The authors attempted to elucidate the deterioration of the breathing transformer oil in actual service using the electric loss index measurements, physical functional properties, and different techniques of spectroscopy. It can be concluded that:

- A definite relationship exists between the oil aging and the dielectric loss index which increases rapidly with the age of oil and provides a reliable picture of oil aging.
- The dielectric loss index ε'', is a weak function of field strength in a range of 1.5 to 10 kV cm^{-1} whereas it is a strong function of temperature and increases exponentially with the elevation of temperature.
- Ferric iron content of aged oil increases conspicuously as compared to Pb^{++} and Cu^{++} and in the presence of humidity plays a dominant role in the chemical interaction and hence oil deterioration.
- Viscosity of the oil decreases with aging, but not very appreciably.
- Carbonyl and polar groups can not be detected in oil using IR, PMR, ^{13}C-NMR and GC spectroscopic methods.

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دراسة تأثير زيت المحولات عمرياً بجهد الاستخدام بطريقة قياسات العزل الكهربي والتحليل الكيميائي الطيفي

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يقدم هذا البحث النتائج العملية لدراسة تأثير شدة المجال الكهربي والحرارة على خواص زيت المحولات من حيث العزل الكهربي والخواص الطبيعية، وأخذت عينات الزيت من محول فائق الضغط العالي كان يعمل لمدة ٧ سنوات.

وتم مقارنة ومناقشة تأثير الترشيح واستخلاص الغازات على هذه الخواص بالنسبة للزيت المستعمل وقرينه الغير مستعمل. وحاول البحث إيجاد ارتباط بين اللزوجة ونسبة الرطوبة ومحتوى «الكاتيون» وبين خواص العزل الكهربي.

بينت النتائج التجريبية أن معامل الفقد لجميع العينات لا يعتمد على شدة المجال ولكن يعتمد على الحرارة ويزداد تبعاً لدالة أسية (e^x). بازدياد درجة الحرارة. ويعد معامل الفقد العزلي مقياساً يعتمد عليه لبيان مدى تشغيل وتحميل الزيت حيث يزداد قيمته مع زمن التشغيل.

إلا أن القياس الطيفي بواسطة الرسم اللوني الغازي

وتحت الحمراء ورنين البروتون المغناطيسي، وكاربون ١٣ رنين النواة المغناطيسي - لم يكشف عن وجود مجموعات «كاربونيل» أو منتوجات قطبية.