

FTIR and X-Ray photoelectron spectral (XPS) evidence for interaction between natural ester and cellulose paper

Sohan Beldar
Savita Oil Technologies
Limited, 17/17A, Thane-
Belapur Road, PO Vashi,
Navi Mumbai 400703, India

Rohit Dolasiya
Savita Oil Technologies
Limited, 17/17A, Thane-
Belapur Road, PO Vashi,
Navi Mumbai 400703, India

Girish Morde
Savita Oil Technologies
Limited, 17/17A, Thane-
Belapur Road, PO Vashi, Navi
Mumbai 400703, India

C.S.Narasimhan*
Savita Oil Technologies
Limited, 17/17A, Thane-
Belapur Road, PO Vashi,
Navi Mumbai 400703, India

ABSTRACT - Several researchers have claimed that Natural Esters enhance the thermal stability of insulation paper. It has been claimed that the chemical interaction accounts for slowing down of ageing of paper and enhancement of insulation life. The enhancement of paper life translates to transformer asset life enhancement. We have conducted aging studies at 120 °C on normal Kraft paper (NKP) as well as thermally upgraded Kraft paper (TUK). The results showed unambiguous development of carbonyl structure on the paper surface – both normal Kraft paper and thermally upgraded paper. These results are further corroborated with X-ray photoelectron spectroscopy (XPS) which lends further support to the formation of carbonyl structure on the paper surface. The results are interpreted in terms of transesterification reaction taking place between cellulosic hydroxyls and the carboxylate of oil.

Keywords — Natural ester fluid (Biotransol-HF), enhancement of insulation life, thermally upgraded Kraft paper, Normal Kraft Paper, transesterification, FTIR, XPS.

I. INTRODUCTION

Natural Esters are increasingly becoming a fluid of choice in transformers, thanks to their excellent fire-safety vis-à-vis mineral oils [1]. The fluid is also preferred at environmentally sensitive areas due to its ready biodegradability and non-toxicity to marine life [2, 3]. Besides these benefits, there is yet another important aspect which is related to performance. This has to do with enhancement of life the of paper insulation [4, 5]. This is a very significant benefit since the life of a transformer asset is predominantly determined by the life of paper insulation [5, 6].

The question is how does the natural ester slow down the ageing of paper compared to mineral oil? To answer this question, a few laboratories have done scientific investigations of the two systems and have come up with a few speculations [1, 2 and 4].

It is in this background that we, at Savita Oil, have undertaken this work. Savita Oil Technologies has developed its own Natural ester, Biotransol HF, and in this paper we report our investigations to explore and find mechanistic pathways contributing to slowing down of ageing of paper in presence of our natural ester.

II. EXPERIMENTAL DETAILS

A. Raw Materials

The insulating liquids used in this experiment were natural ester (Biotransol HF, hereinafter referred to as Biotransol) and mineral oil (Transol). Thermally upgraded Kraft paper (hereinafter referred to as TUK, Make - Weidman 22 HCC Insuldur of thickness - 0.09 mm and width - 25.35 mm.) and normal Kraft paper (hereinafter referred to as NKP, Make - Weidman of thickness 0.17 mm and width – 29.18 mm). The initial moisture content of both papers was maintained as per IEEE C57.100 – 2011 (about 0.25% to 0.5% by weight) [6].

B. Experimental set-up (Sealed Tube Reactor)

The Stainless Steel-316 sealed tube reactors are made as per dimensions provided in IEEE C57.100 –2011 [6]. The reactor is provided with two valves – one for

purging of nitrogen with dip tube and the other for vacuum and nitrogen venting. Pressure gauge is provided to monitor the pressure of reactor. The reactor is kept inside an electrically heated hot air oven for the duration of experiment. The fig.1 shows the reactor used. On completion of experiment kraft paper was degreased by n-Hexane (4 to 6 times). Spectroscopic analysis of degreased Kraft paper was done by FTIR and XPS [7].



Fig. 1 Sealed tube reactor as per IEEE C57.100-2011

C. FTIR Spectroscopy

An ALPHA-ATR FTIR Spectrometer (Make - Bruker) was used in this experiment to get infrared spectrum of functional groups of paper insulation. The attenuated total reflection (ATR – Diamond) technique was used to get the infrared spectra [8]. Paper samples are placed in the path of an infrared beam will absorb and transmit light and the transmitted light signal is detected by the detector. This measurement needs only a small sample of insulating paper. In order to enhance the signal strength, the paper was folded 3 to 5 times before FTIR analysis. The FTIR wavelength range of 4000 – 540 cm^{-1} was scanned for the reported spectra (in the transmission mode) [8].

D. XPS (X-ray photoelectron spectroscopy):

A K-Alpha XPS spectrometer (Make - Thermo Scientific) was used for surface analysis of the new and aged papers [9]. In the XPS technique, an X-ray photon is used to knock off an electron from an inner orbital, say C1s in the case of carbon and the binding energy of the electron emitted is measured in a detector [9, 10]. Chemical shifts in the binding energy of an element are associated with a particular chemical structure. For instance, Carbon 1s electron binding energy is sensitive to its environment and changes depending on its presence as carbonyl or ether etc. [9, 10].

III. RESULTS & DISCUSSIONS

A. Results of FTIR

FTIR spectra were taken for the aged samples to see if any chemical interaction has taken place between the free carboxylic acid in the natural ester Biotransol and the cellulose -OH groups of Kraft paper. Interestingly, the fig. 2 (a) (b) and 3 (a) (b) show that after 264 hrs of ageing of both Kraft papers (NKP and TUK) in Biotransol at 120⁰C, the paper surfaces exhibit an absorption peak at 1743 cm^{-1} . This peak clearly indicates the presence of a carbonyl group. The fresh papers (NKP and TUK) did not show any peak at 1743 cm^{-1} .

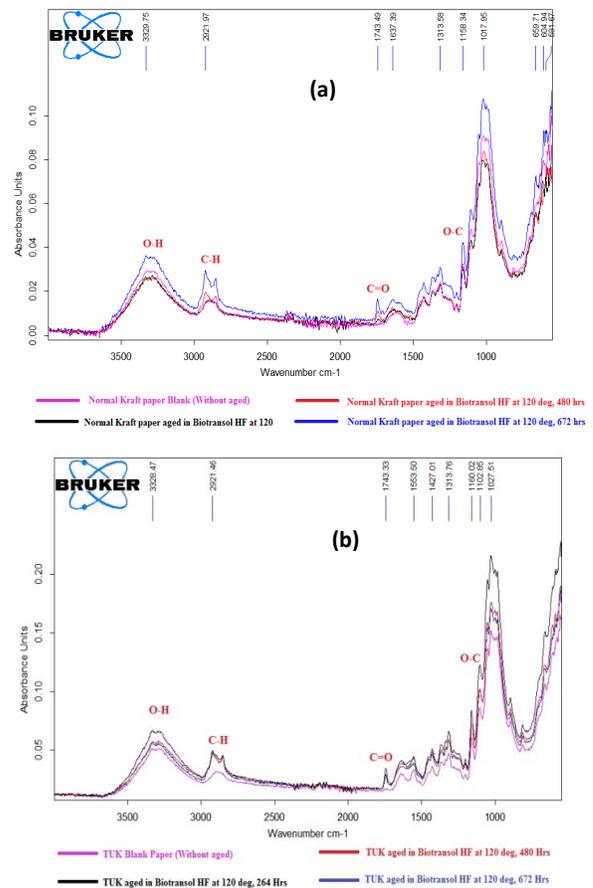


Fig. 2 (a) and 2 (b) FTIR spectra of NKP and TUK respectively aged in Biotransol at 120⁰C for different time intervals.

Fig. 3 (a) and 3 (b) show expanded view of FTIR spectra on NKP and TUK aged for different periods of time. The FTIR spectra in each fig. are shown for four different samples – one for fresh paper and three for papers aged for different periods of time in biotransol. All the aged samples consistently show peaks at 1743 cm^{-1} corresponding to carbonyl group.

Further, there is clear increase in 1743 cm^{-1} peak strength as the time of ageing increases.

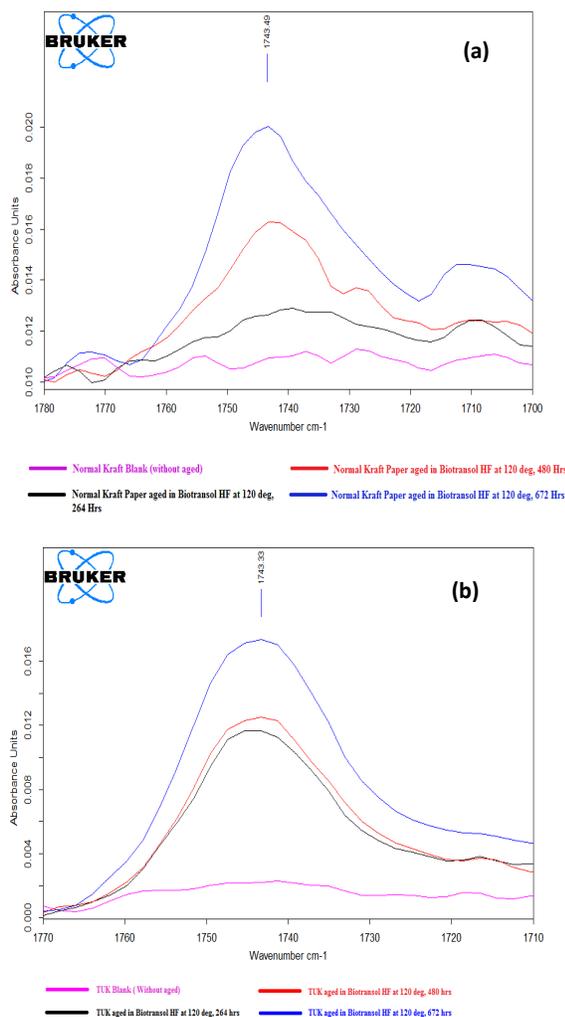


Fig. 3 (a) and 3 (b) FTIR spectra at 1743 cm^{-1} wavelength of NKP and TUK in Biotransol aged at 120°C at different time intervals.

B. Results of XPS

XPS is a powerful surface spectroscopy and can unambiguously identify and even quantify surface functional groups [8]. The results of this spectroscopy are shown on fresh NKP and TUK papers along with the paper samples aged at 120°C for 672 hours in biotransol. The table 1 shows the binding energy values taken from literature for C1s electron in various chemical environments [9, 10]:

Table 1 Binding energies of common chemical states

Chemical state	Binding energy (C1s/eV)
C-C	284.8
C-O-C	~286
O-C=O	~288.5

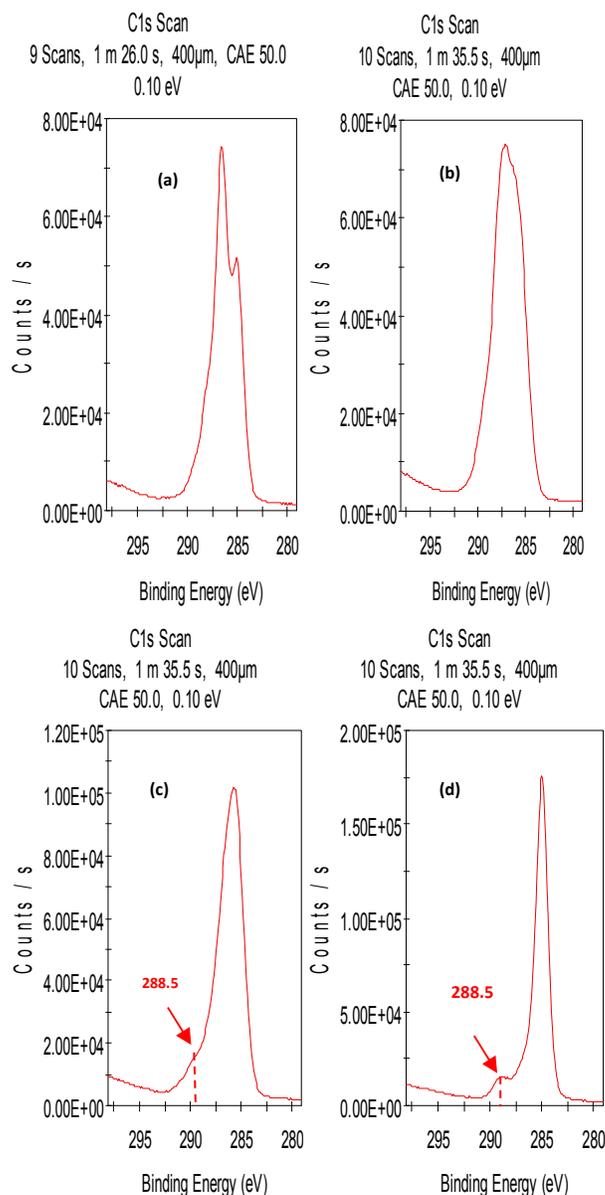


Fig. 4 (a) and 4 (b) are XPS Spectra of fresh NKP and fresh TUK, Fig. 4 (c) and 4 (d) are XPS spectra of NKP and TUK aged at 120°C for 672hrs.

It may be seen from the fig. 4 (a) and 4 (b) that none of the two fresh papers (NKP and TUK) show any peak at binding energy of 288.5 eV . On the other hand, the corresponding aged papers (aged at 120°C for 672 hours) show peaks at binding energy of 288.5 eV . The peak at 288.5 C1s/eV is

attributed to carbonyl chemical shift. The interpretations are based on literature published for XPS of carbonyl structures [9, 10].

IV. Suggested mechanism for paper life enhancement:

It must be pointed out that mineral oil-aged papers did not show carbonyl related peaks either in FTIR or in XPS. Therefore, it is safe to conclude that the 1743cm^{-1} peak in FTIR spectra of fig. 3 and 288.5 eV peak of XPS spectra of fig. 4 are due to the formation of ester group on the paper surface. This could be caused by transesterification of cellulosic hydroxyl groups with the carboxylate group of free fatty acids of the natural ester Biotransol. This is shown schematically in the fig. 5 [7]:

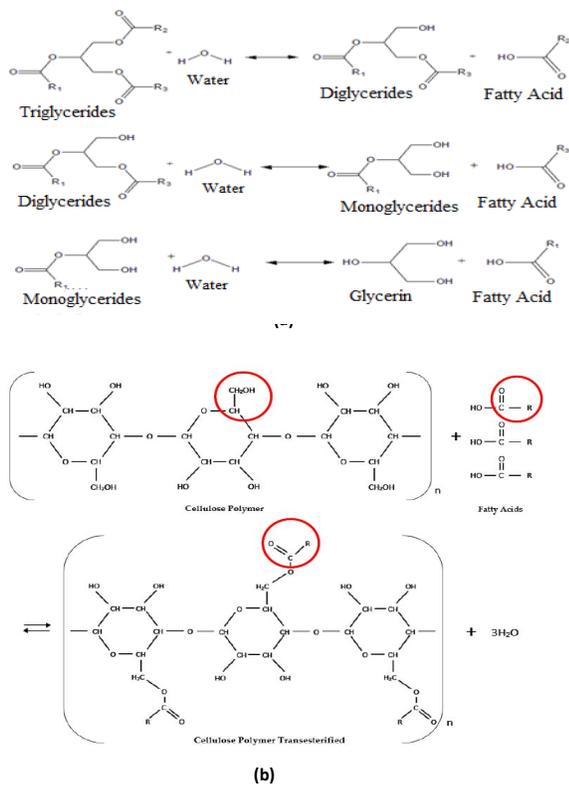


Fig. 5 (a) Hydrolysis of Natural Ester and Fig. 5 (b) Transesterification process of cellulose paper.

Transesterification is expected to enhance paper life in two specific ways: 1) It increases the average molecular weight of cellulose due to attachment of long C18 chain on the cellulose hydroxyls. 2) Secondly, transesterification will also result in enhanced hydrophobicity of the paper due to the presence of a long chain fatty acid, typically made up of C18. (A more hydrophobic paper should last longer than a hydrophilic paper).

V. SUMMARY & CONCLUSIONS

A study was carried out on our natural ester fluid Biotransol in order to understand how the ester fluid enhances the life of paper insulation in comparison to conventional mineral oils. The study involved sealed tube experiments conducted at 120degC over a period of time with Biotransol. FTIR and XPS spectroscopic evidences were presented to propose interaction between cellulosic hydroxyls and the carboxylate of fatty acids from natural ester. It is concluded that transesterification reactions contribute to strengthening of the paper and slowing down the aging of Kraft paper in natural ester fluid. Transesterification will also result in enhanced hydrophobicity of the paper due to the presence of a long chain fatty acid, typically made up of C18. Further detailed studies of XPS are being planned for the future.

REFERENCES

- [1] Prof. Giovanni Dotelli, "Comparative Investigation on the Properties of Transformer-used High-temperature Resistant Oil and Paper Insulation Materials" (Anno Accademico 2015-2016).
- [2] J-C DUART *, L. C. BATES, E. W. KEY, R. ASANO JR, L. CHEIM, E. W. KEY, D. B. CHERRY C., C. CLAIBORNE, Thermal Aging Study of Cellulosic Materials in Natural Ester Liquid for Hybrid Insulation Systems (D1-111, CIGRE 2012).
- [3] Technical brochure 436, Work group A2.35, Experiences in Service with New Insulating Liquids (CIGRE October 2010).
- [4] L. Yang, R. Liao, S. Caixin, M. Zhu, Influence of vegetable oil on the thermal aging of transformer paper and its mechanism, IEEE Trans. Dielectric. Electric. Insulation 18 (2011) 692-700. DOI: 10.1109/TDEI.2011.5931054.
- [5] C. Patrick McShane, Kevin J. Rapp, Jerry L. Corkran, Gary A. Gauger, John Luksch, Aging of Paper Insulation in Natural Ester Dielectric Fluid (2001 IEEE/PES Transmission & Distribution Conference & Exposition, Oct. 28 - Nov. 02, 2001, Atlanta GA).
- [6] IEEE C57.100-2011 - IEEE Standard Test Procedure for Thermal Evaluation of Insulation Systems for Liquid-Immersed Distribution and Power Transformers, IEEE: New York, NY, USA, 2011.
- [7] Abi Munajad*, Cahyo Subroto and Suwarno, Study on the Effects of Thermal Aging on Insulating Paper for High Voltage Transformer Composite with Natural Ester from Palm Oil Using Fourier Transform Infrared Spectroscopy (FTIR) and Energy Dispersive X-ray Spectroscopy (EDS) (School of Electrical Engineering and Informatics, Institute Technology Bandung, 40132 Bandung, Indonesia, Received: 16 October 2017; Accepted: 8 November 2017; Published: 13 November 2017).
- [8] ALPHA FTIR (ATIR) manual, Bruker
- [9] Thermo fisher technical brochure, Binding energies values of different functionalities.
- [10] Thermo fisher application notes on carbon C1s (non metal).