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Efficacy of Polyphosphoric Acid in Reducing the Degree of Thermal Aging of Agbabu Natural Bitumen

[1*]Bakare Hassan O. & [1]Olabemiwo Ojeyemi M.

[1]Department of Pure and Applied Chemistry,Faculty of Pure and Applied Sciences,
Ladoke Akintola University of Technology (LAUTECH), Ogbomoso, Nigeria
bakarehassanabuja@yahoo.com

***Absract*:** Bitumen is a complex mixture of hydrocarbons which occurred naturally or obtained from crude oil distillation. The degradation of bitumen causes its rapid aging leading to deterioration of asphalt based pavement readily induced by cracking, rutting, potholes etc. Aging in bitumen is attributed to chemical oxidation of its molecules and exposure to environmental factors, such as heat, moisture and sunlight. This study therefore investigates the viability of using polyphosphoric acid (PPA) to reduce the oxidative degradation effect of heat (60^{o}C) on constituents of Agbabu natural bitumen (ANB) with a view to making it more durable when used for road pavement. Modification of ANB with PPA was carried out at 150-55^{o}C using melt blend technique. Thereafter, the PPA modified and neat (unmodified) ANB samples were thermally aged in a hot air oven at 60^{o}C. Fourier Transform Infrared (FTIR) Spectroscopy was used to evaluate the changes in the structure of ANB and aging indexes of neat and PPA modified samples of ANB were calculated. The neat and PPA modified ANB samples aged as a result of their exposure to temperature at 60^{o}C. However, the aging indexes of PPA modified samples of ANB were found to be lower compared with that of the neat sample of ANB. This implies that the rate of aging (60^{o}C) of the neat ANB was faster than that of PPA modified ANB samples. Thus, a good potential for reducing thermal aging in ANB was found in PPA.

***Keywords*:** Agbabu natural bitumen, Polyphosphoric acid, FTIR analysis, Aging, Oxidative degradation

1.0 Introduction

Flexible road pavement (FRP) is made up of bitumen, mineral aggregate, filler and additives. It is a known fact that FRP deteriorates with time as a result of usage and contact with some environmental factors, such as heat, moisture, sunlight etc. The chemical oxidation of bitumen molecules and interaction with some environmental factors leads to aging of bitumen which manifests in pavement surface distresses such as cracks, rutting, potholes, ravelling etc.

Reduction of the rate of bitumen aging has been a challenge and the incorporation of materials such as polymers, wastes, PPA etc into the matrix of bitumen for this is well reported in the literatures (Iliya and Adam, 2011; Shulga *et al.*, 2012). The incorporation of materials such as polymers into bitumen is known as bitumen modification, and the objective of this study is to reduce the susceptibility of bitumen molecules to oxidation and thus increase aging resistance of the bitumen.

The application of PPA in modification of bitumen has been the usual practice as far back as 1939 (Burke *et al*., 1939). Daranga *et al., (*2009) used PPA to modify some binders and reported an increase in stiffness and reduction in oxidation process in the modified binders. Similarly, the study of Masson and Collins, (2009) showed that PPA modified asphalt when used in road pavement led to increase in pavement upper service temperatures and reduction of rutting. A mixture of PPA and SBR was used by Feng and Jianyin, (2010) to modify asphalt. An improvement in some physical properties and rheological properties of the modified asphalt was reported by these authors.

Bitumen aging has been identified as the major factor responsible for deplorable condition of our roads (Sa Araujo, 2013). Two aging mechanisms have been identified, which are reversible and irreversible mechanisms. The reversible mechanism (physical hardening) is revocable by application of heat and occurs as a result of molecular re-organisation in bitumen which is a function of time (Tabatabaee *et al.,* 2012). The irreversible mechanism occurs as a result of oxidation, dehydrogenation, polymerisation and condensation reactions and it is accompanied with loss of volatile components. It is either thermally induced by heating or light induced by exposing modified or unmodified bitumen sample to sunlight or ultra violet (UV) radiation (Mouillet *et al.*, 2008; Lins *et al.*, 2008).

Oxidative aging causes hardening of bitumen and occurs throughout the service life (Chen and Huang, 2000). It is induced by the chemical reaction of bitumen molecules with oxygen. Xiaohu *et al.,* (2008) carried out investigation on how different laboratory aging tests, viz: Rolling Thin Film Oven Test (RTFOT), Pressure aging Vessel (PAV) Test and Rotating Cylinder Aging Test (RCAT) under various conditions relate to field aging of bituminous binders. They concluded that the field aged bitumens showed a much higher level of sulphoxides but lower level of carbonyls compared to laboratory aging. The reason for this according to the authors was that higher temperature in laboratory aging results in higher amount of carbonyls while longer time in the field produces higher amount of sulphoxides. It was also concluded that aging kinetics and formation of sulphoxides and carbonyls were strongly temperature dependent. For the SBS modified binder, the polymer was found to inhibit the formation of sulphoxides on aging.

Most of the studies on application of PPA to modifying bitumen were based on artificial or petroleum bitumen. There is paucity of literatures on the use of PPA to modify natural bitumen and ANB. Crude petroleum/oil or natural bitumen is not uniform in composition as its composition varies from well to well (Amit, 2010). The implication of this is that crude petroleum/oil or natural bitumen, depending on the source behaves differently to modifiers. Therefore, it was decided to investigate the viability of using PPA to modify the ANB with a view to improve its service life by making it less susceptible to relatively high road pavement temperature.

2.0 Methodology

2.1 Materials

2.1.1 Bitumen

The bitumen used in this study was natural bitumen sample collected from one of the observatory wells sunk by the Nigerian Bitumen Corporation (NBC -7) located opposite Saint Stephen's Primary School, Agbabu, Ondo State, Nigeria. Agbabu is located on the so called bitumen belt of south-western Nigeria. The belt has geographical location of Longitude 3^o45’E and 5^o45’E and Latitude 6^o00’N and 7^o00’N and spans across Edo, Ondo and Ogun States of Nigeria (Fagbote *et al.,* 2012).

2.1.2 Polymers

The modifier used in this study was Polyphosphoric acid (PPA) with concentration of 105% phosphoric acid (75.9% P_2O_5). The specific gravity is 2.05.

2.2 Extraction of Moisture from Bitumen Sample

Method described by Vernon and Katy (1999) was modified and employed for extracting moisture from ANB (Bakare *et al.,* 2015). Calcium chloride granular salt was mixed with bitumen sample and heated to 65^oC in an oven to get rid of moisture. Meanwhile, the moisture content was monitored using infrared moisture analyser (Sartorius AG Germany), MA 35M-00023012 until it was approximately zero.

2.3 Purification of Bitumen Sample

The Bitumen sample was purified using the modified method of Rubinstein and Strausz, (1979). The mixture of 1000 cm^3 chloroform and 100 g of natural bitumen sample was stirred with a glass rod to complete dissolution. The bitumen in the filtrate was then recovered by vacuum evaporation of the solvent using rotary evaporator.

2.4 Preparation of PPA modified ANB

The raw natural bitumen sample collected from Agbabu was dehydrated and then purified as described in our previous study (Olabemiwo *et al.,* 2015). Melt blend technique was used for preparation of the PPA modified samples via a high shear mixer. 400 g of ANB was heated to a temperature range of 150-155^oC in an iron container. Then, PPA was gradually added. Mixing continued at 150-155^oC temperature range with the speed of the mixer also maintained at 1200 rpm for 1hr to obtain a homogenous mixture. The percentage composition of PPA by weight of bitumen used for blending varied from 2 to 6%.

2.5 Aging Simulation of Unmodified and Modified ANB Samples

2.5.1 Thermal Aging Using Oven

Thermal ageing was simulated by weighing 5 g of the modified bitumen sample into a Pyrex glass Petri dish to a thickness of 0.1 cm. The dish was then set in a hot air oven at 60^oC for three weeks. 0.4 g of the sample was withdrawn periodically from the oven at interval of one week and conditioned to room temperature for FTIR analysis to study the sample's degradation due to heat at 60°C (Olabemiwo *et al*., 2010).

2.6 FTIR Analysis of Aged Unmodified and Modified ANB Samples

Fourier Transform Infrared (FTIR) Spectrophotometer FTIR-8400s, SHIMADZU, with Spectra range: 4,000-400 cm^{-1} was used. The IR spectra of aged modified and unmodified samples were generated by scanning each sample. 1.5 mg of the sample was ground with 150 mg of analytical grade potassium bromide. The mixture was pressed in a hydraulic press to form a pellet. The pellet was mounted on the instrument and the infrared spectra of modified and unmodified samples were generated by separately scanning each sample (4000-400 cm^{-1}) on Fourier Transform Infrared Spectrophotometer. Calculations of functional and structural indexes for the bands were based on the equations proposed by Mouillet *et al*., (2008).

. $Sulphoxide = \frac{A_{1030}}{\sum A}$;……………………………………(Equation 1)

- The sum of the area represents $(\sum A) = A_{1700} + A_{1600} + A_{1460} + A_{1376}$

. $+A_{1030} + A_{864} + A_{814} + A_{743} + A_{724} + A_{(2953,2923,2862)}$ …. (Equation 2)

3.0 Results and Discussion

3.1 FTIR Analyses of PPA Modified and Unmodified ANB Samples

The FTIR spectra of unmodified and modified Agbabu natural bitumen were recorded in the range of 4000-400 cm^{-1} as shown in Figure 1.0 and Figures 2.0(a-c) respectively.

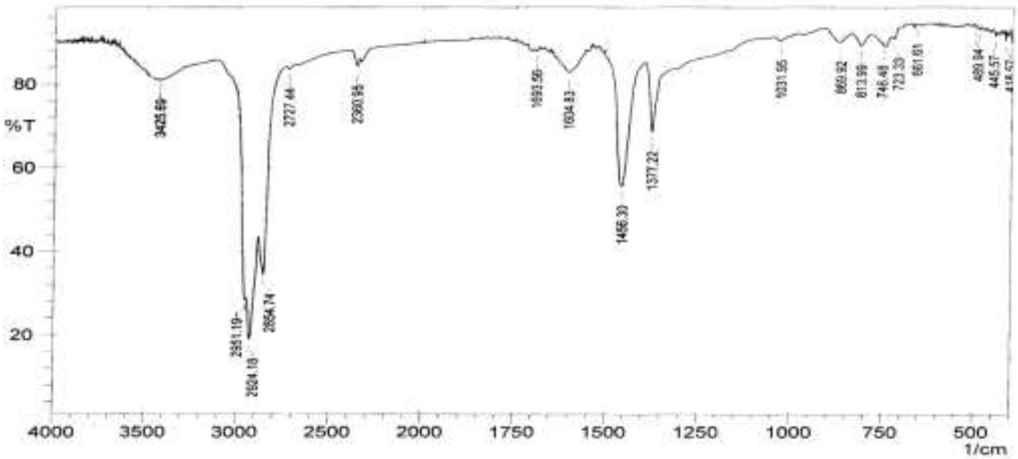

Figure 1.0: FTIR of Unmodified ANB

The peaks obtained in the FTIR spectrum of unmodified ANB are similar to the ones identified by Lamontagne *et al.,* (2001). In their study, they identified absorption bands related to asphalt binder of grade of PG 64-22 to include 2922 cm^{-1}(υ_{as} CH_2 CH_3), 2882 cm^{-1}(υ_s CH_2 CH_3), 1601 cm^{-1}(υ C=C), 1455 cm^{-1} (υ_{as} CH_3 deformation) , 1376 cm^{-1} (υ_s CH_3 deformation), 1031 cm^{-1} (υ SO2), 868 cm^{-1}, 813 cm^{-1}, 747 cm^{-1}(C-H aromatics), and 722 cm^{-1} (alkyl chain). Assignment of functional groups in the unmodified ANB is as described in our previous studies (Olabemiwo *et al.*, 2016).

The comparison of peak positions and intensities of various peaks appearing in the infrared spectra of the base bitumen, Figure 1.0 and PPA modified ANB (containing 2, 4, and 6% PPA compositions), Figure 2.0(a-c) revealed that there is appearance of additional new peaks with wave numbers in the ranges of 999-1006 cm^{-1} for P-O-P stretching and 497-500 cm^{-1} for P-O-P bending vibration in the spectra of PPA modified ANB samples. This indicates that the PPA has undergone some type of interactions with bitumen resulting in structural changes in the modified bitumen. There is no noticeable disappearance of prominent infrared peaks, in contrast to findings of Gupta *et al.*, (2012) who reported disappearance of some prominent infrared peaks in modified bitumen. However, peak shifting occurred in the infrared spectra of PPA modified ANB samples prepared in this study. Changqing *et al.* (2012) reported that asphalt experienced no obvious changes in functional groups before and after modification. This suggests that the modification of asphalt with PPA is a physical process.

Some similarities in the PPA modified ANB spectrum were noted with the submission of Feng and Jianyin, (2010) on major spectrum of PPA who reported infrared absorption peaks to include 1012 cm^{-1}, 933 cm^{-1}, 772 cm^{-1}, and 478 cm^{-1} as shown in Figure 3.0. However, P-O-P asymmetric vibration at 933 and 773 cm^{-1} were absent in the spectra of PPA modified ANB samples.

Furthermore, the infrared spectra of PPA modified samples showed that sulphoxide bands were absent, which is in agreement with the findings of Masson and Collins, (2009). Their finding showed that sulphide groups (aliphatic or aromatic), was inert when heated with PPA at 150°C for 1 hour i.e. the aliphatic or aromatic sulphur compounds did not react with PPA during blending.

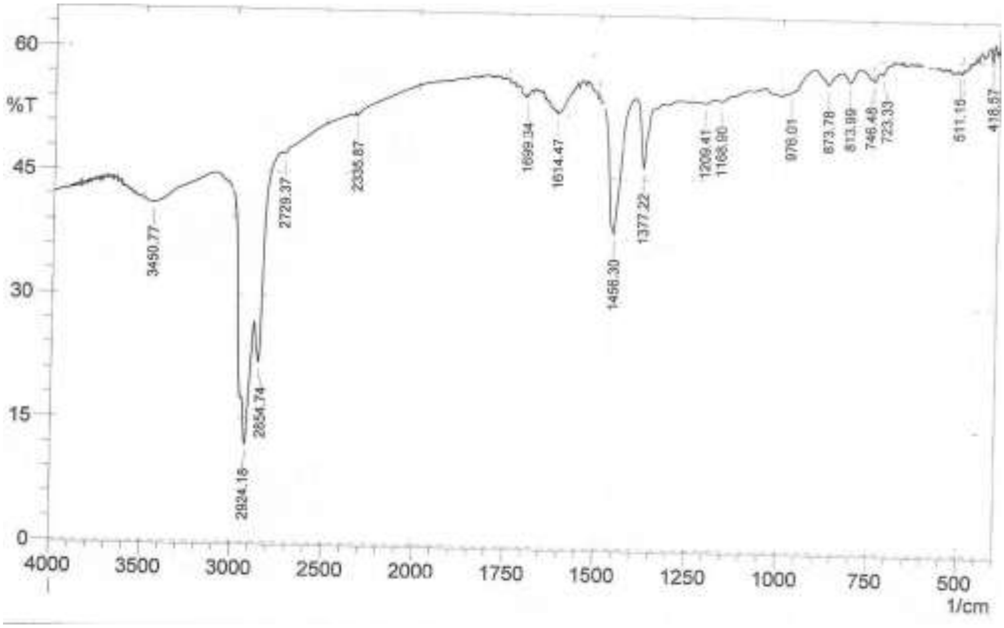

Figure 2.0 (a): FTIR Spectrum of 2% PPA Modified ANB

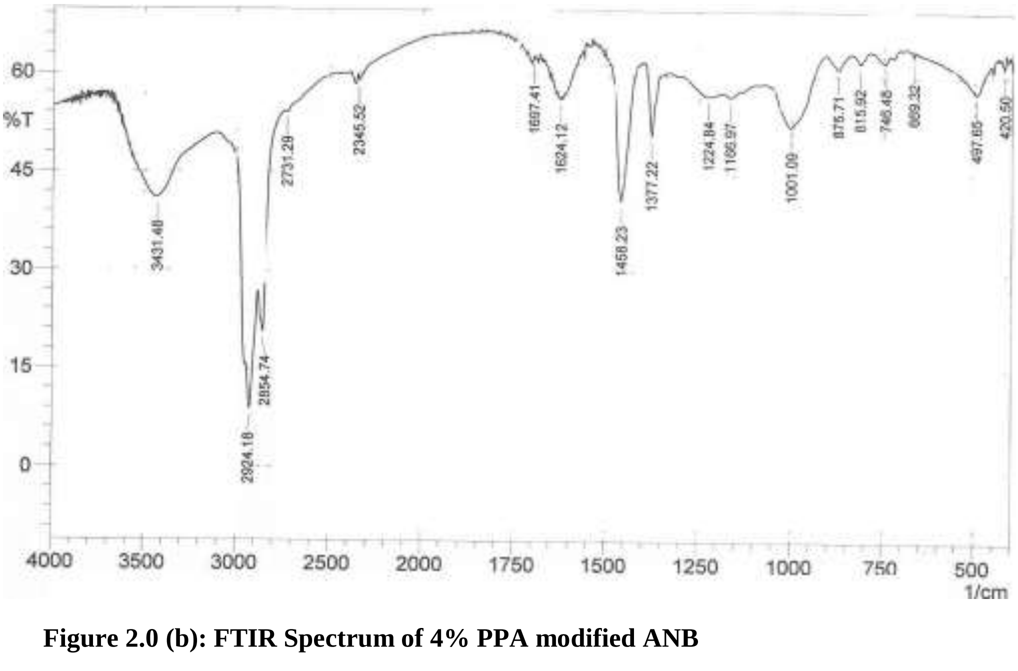

Figure 2.0 (b): FTIR Spectrum of 4% PPA modified ANB

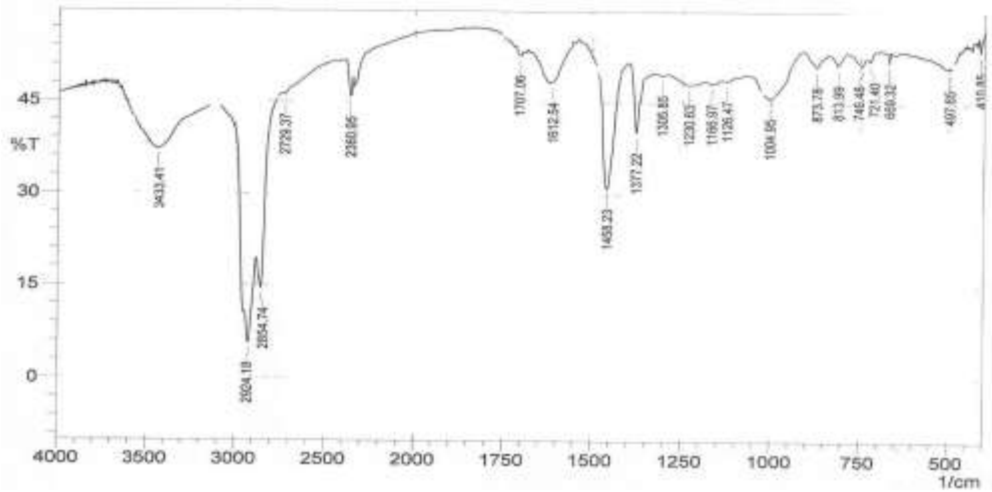

Figure 2.0 (c): FTIR Spectrum of 6% PPA Modified ANB Modified

3.2 FTIR Analyses of Thermal Aged Modified and Unmodified ANB Samples

The FTIR spectra of aged modified and unmodified ANB samples are as shown in Figures 3.0(a-l). The FTIR test was carried out to detect the effect of aging on the areas of absorption peaks as well as absorption peak wave numbers present in the unmodified and modified ANB samples. The PPA modified and unmodified ANB samples were subjected to thermal aging using oven at 60°C for a period of three weeks

Petersen and Harnsberger, (1998) reported that aging was responsible for shifting in absorption peaks wave numbers observed in neat ANB with intensities/transmittances of these peaks varied with no regular pattern. The shift in some peak wave numbers and transmittances may be due to oxidation of benzylic carbon or benzylic compounds in bitumen. This formed hydroperoxide or peroxy radicals capable of reacting with aliphatic sulphides to produce sulphoxide or undergo non radical self (condensation) reaction to form ketones. The amount of ketones formed on non-benzylic carbon was reported to be small (Petersen and Harnsberger, 1998).

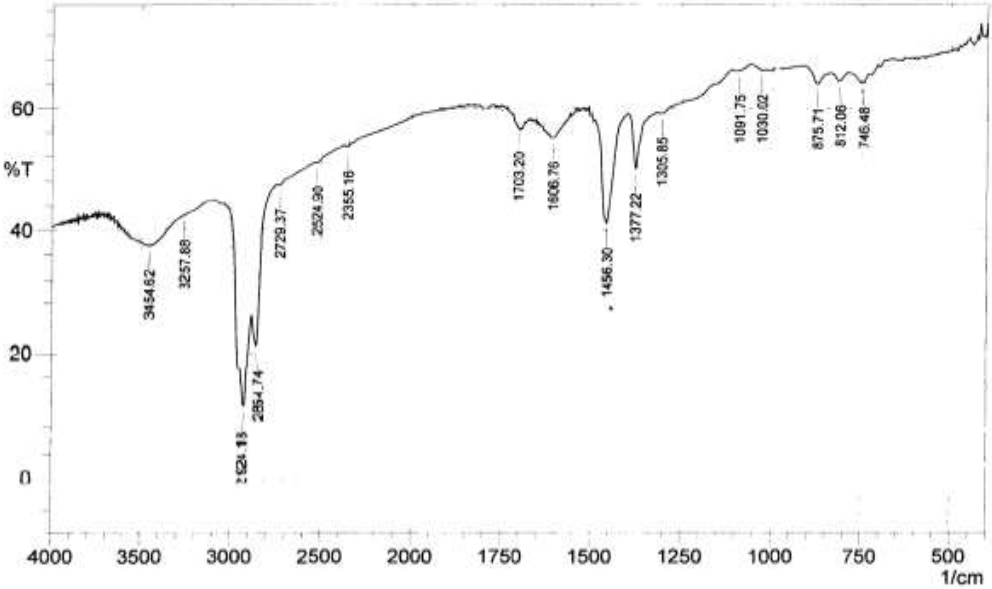

Figure 3.0 (a): FTIR Spectrum of Unmodified ANB Aged with Oven for one Week

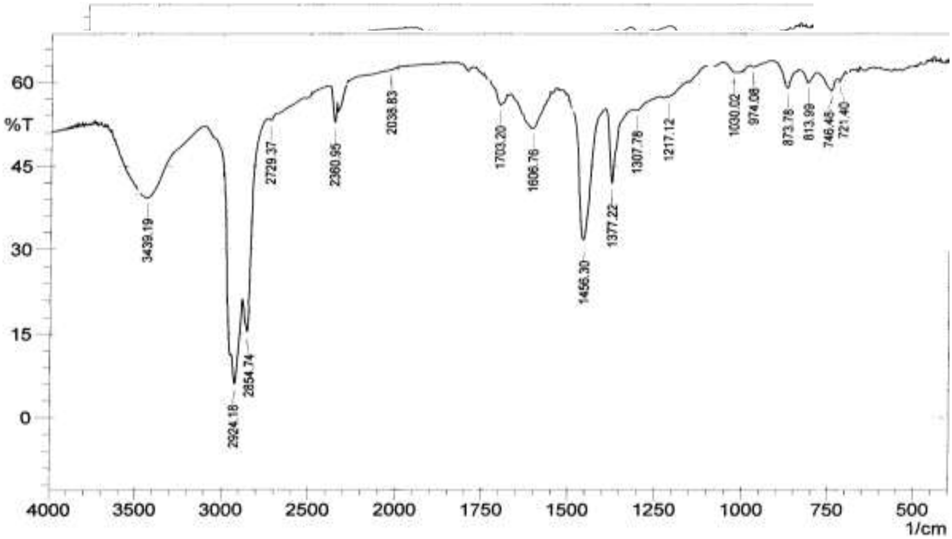

Figure 3.0 (b): FTIR Spectrum of Unmodified ANB Aged with Oven for Two Week

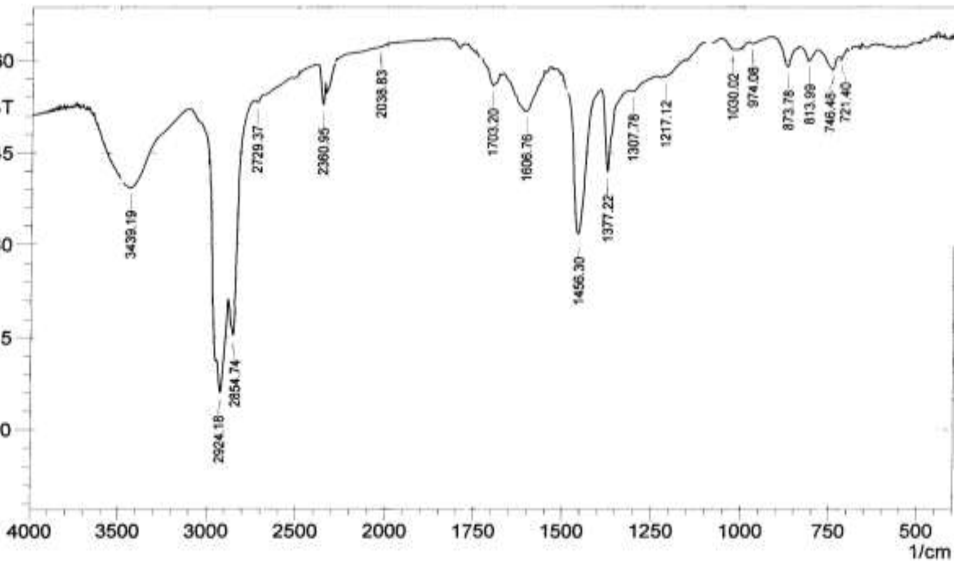

Figure 3.0 (c): FTIR Spectrum of Unmodified ANB Aged with Oven for Three Weeks

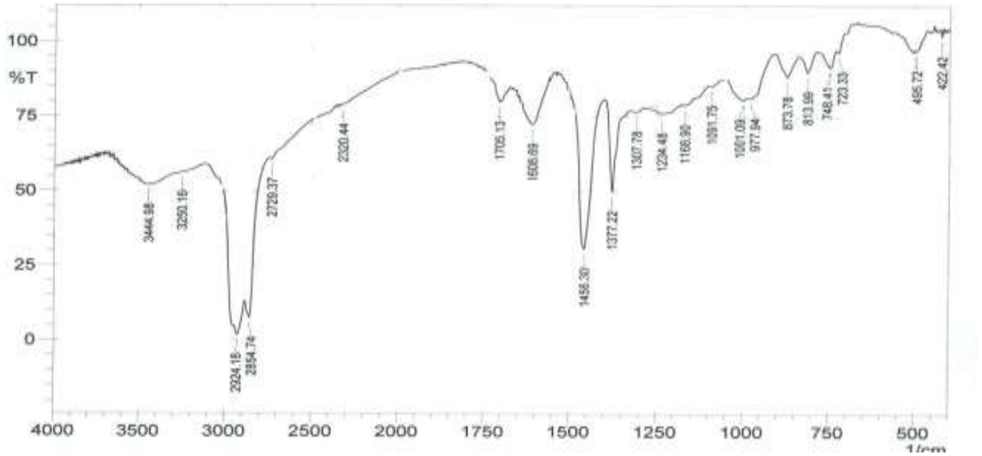

Figure 3.0 (d): FTIR Spectrum of 2% PPA Modified ANB Aged with Oven for one Week

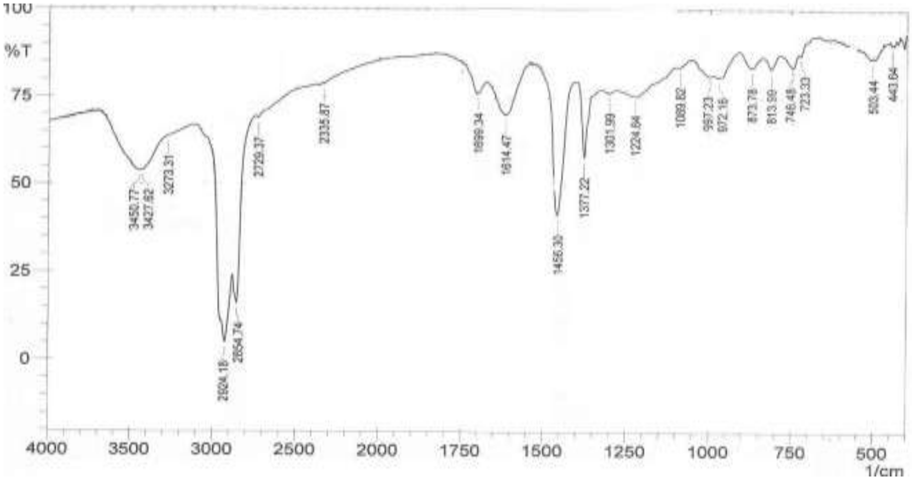

Figure 3.0 (e): FTIR Spectrum of 2% PPA Modified ANB Aged with Oven for Two Weeks

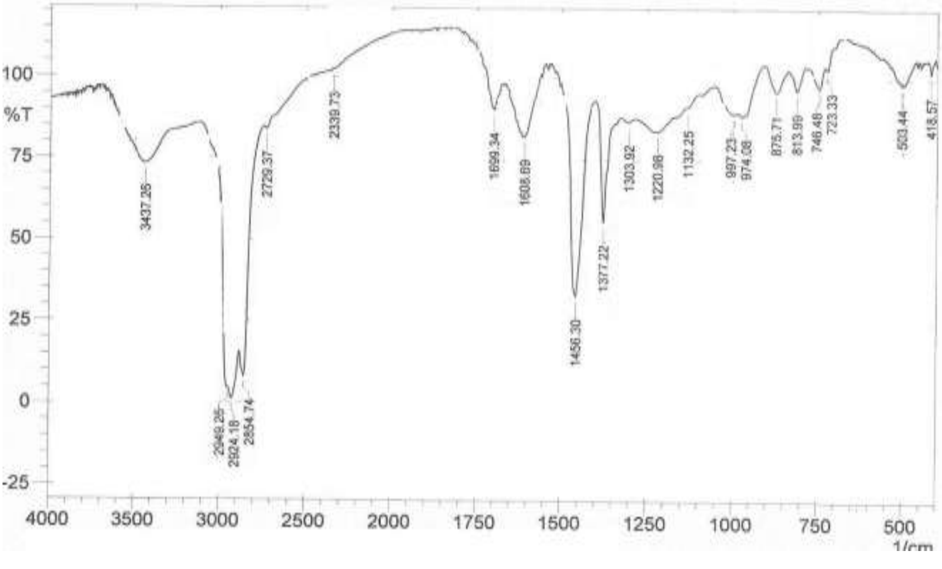

Figure 3.0 (f): FTIR Spectrum of `2% PPA Modified ANB Aged with Oven for Three Weeks

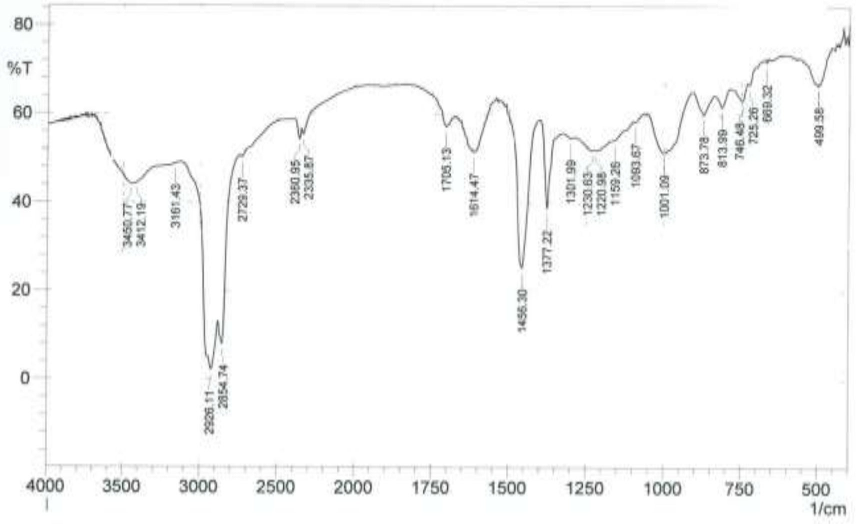

Figure 3.0 (g): FTIR Spectrum of 4% PPA Modified ANB Aged with Oven for One Week

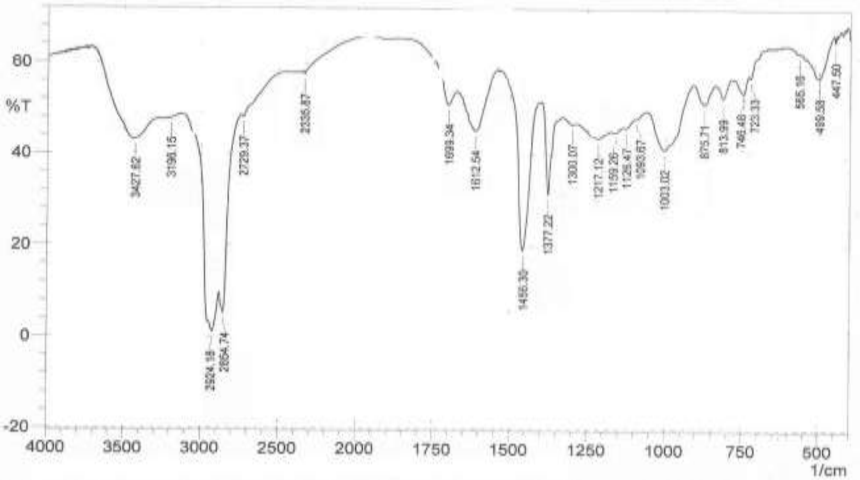

Figure 3.0 (h): FTIR Spectrum of 4% PPA Modified ANB Aged with Oven for Two Weeks

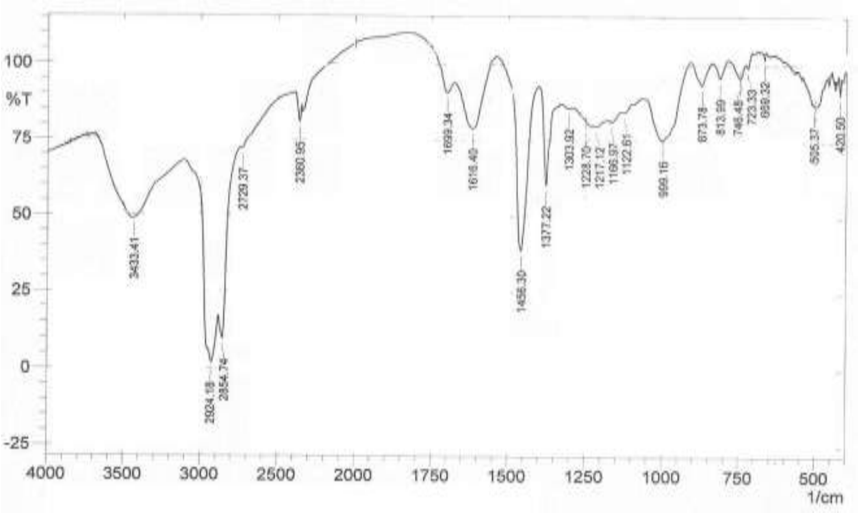

Figure 3.0 (i): FTIR Spectrum of `4% PPA Modified ANB Aged with Oven for Three Weeks

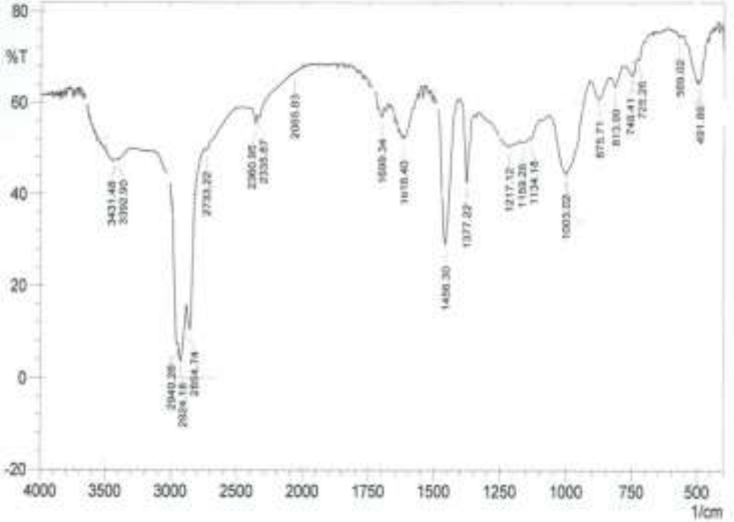

Figure 3.0 (j): FTIR Spectrum of 6% PPA Modified ANB with Oven for One Week

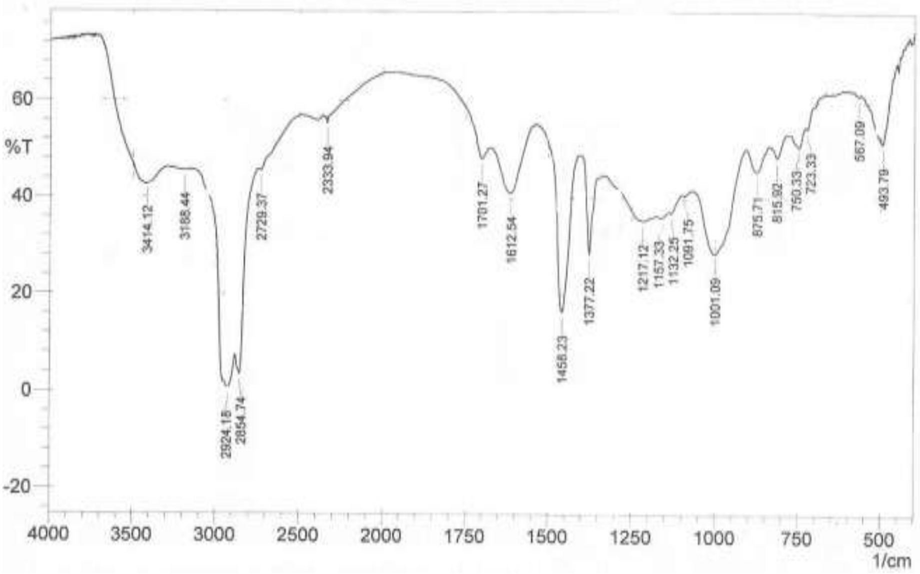

Figure 3.0 (k): FTIR Spectrum of 6% PPA Modified ANB with Oven for Two Week

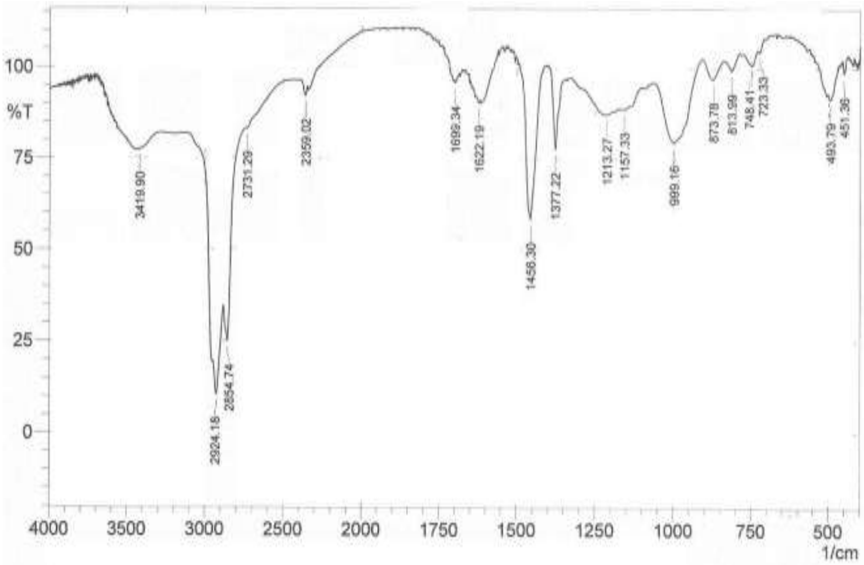

Figure 3.0 (l): FTIR Spectrum of 6% PPA Modified ANB Aged with Oven for 3 Weeks

3.3 Carbonyl indexes of thermal aged modified and unmodified ANB

The plot of carbonyl index as a function of the aging period of thermal aged PPA modified ANB is as shown in Figures 4.0. To quantify the effect of modified samples on reducing the aging of ANB, the carbonyl indexes were calculated for both modified and unmodified samples using the formula of Mouillet *et al*., (2008) in Equations 1 and 2. This is by measuring areas of the FTIR bands to assess the relative amounts of carbonyl compounds formed on aging. The infrared absorbance peak at about 1,700 cm^{-1} is attributed to C=O stretch in carbonyl compounds, such as ketones, carboxylic acids and anhydrides.

The plot of carbonyl index showed that there was growth in the sizes (areas) of carbonyl peaks after aging which was found to be dependent on the period of aging. However, the carbonyl index increased in both modified and unmodified ANB with the aging period due to reaction of bitumen molecules (carbon compounds) with oxygen. The rate of increase in the index (carbonyl) is higher in neat ANB than the modified sample. This is in line with the earlier submission by Lamontagne *et al.,* (2001) that the effect of aging was more considerable in the unmodified ANB compared to that of polymer modified ANB at different aging period as high values of carbonyl and sulphoxide indexes imply high degree of aging effect and vice versa. Similarly, Seyed, (2012) in his study reported that FTIR spectra of unmodified and SBS modified samples showed that aging caused oxidation of bitumen and formed the carbonyl and sulphoxide structures in bitumen. Aging in modified bitumen by SBS has been less than base bitumen.

Hardening of bitumen occurs as a result of oxidation and loss of volatile components. The degree of hardening decreases with increasing percentage of PPA content in the ANB in this study. The plot of sulphoxide index against aging period could not be established for the aged PPA modified samples because FTIR analysis for aged PPA modified samples did not show values for sulphoxide peak as reported by Masson and Collins, (2009). Baumgardner, (2009) also reported that PPA acid when used to modified bitumen actually has anti-oxidative characteristics.

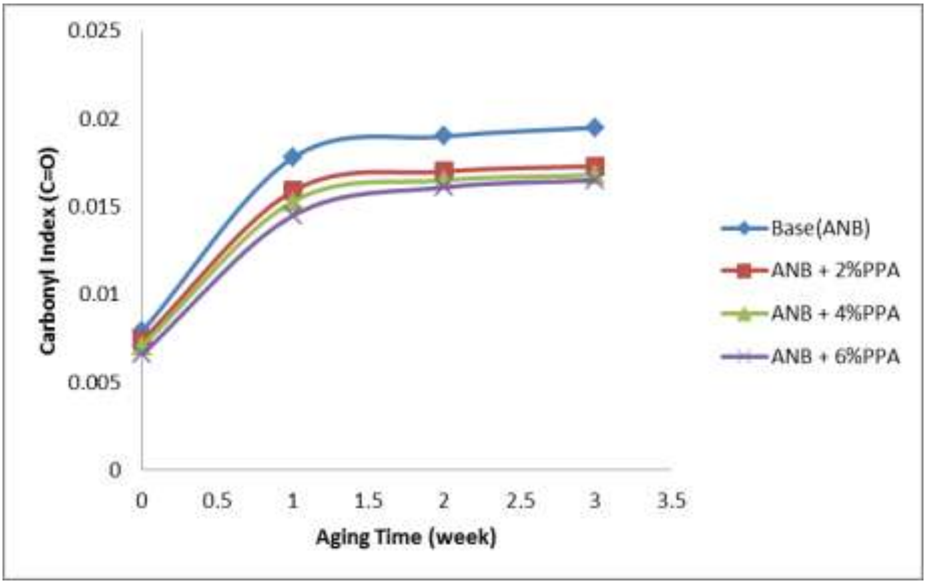

Figure 4.0: Variation of Carbonyl Index of PPA Modified and Unmodified ANB Samples with Period of Light Aging at 60^{o}C

4.0 Conclusion

Samples of ANB modified with PPA were thermally aged (60^{o}C) for a period of three weeks. The infrared spectra of PPA modified ANB samples show carbonyl peak but did not show sulphoxide peak. In addition, the carbonyl index values for PPA modified ANB samples are lower at different aging periods compared to that of unmodified ANB. These imply that sulphur compounds (e.g. sulphides) in ANB are completely inert to oxidants in presence of PPA and also the addition of PPA has improved the aging resistance of ANB to certain degree. The aging resistance of the modified ANB samples is found to increase as the amount of PPA incorporated into ANB increased.

5.0 Acknowledgment

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References

[1] Amit, K. (2010). Physical and Chemical Aging Behavior of Asphalt Cements from Two Northern Ontario Pavement Trials, *Queen's University Kingston, Ontario, Canada*, 1-109.

[2] Bakare, H. O.; Esan, A. O. and Olabemiwo, O. M. (2015). Characterisation of Agbabu Natural Bitumen and Its Fractions Using

Fourier Transform Infrared Spectrometry, *J. of Chemical and Mater. Res.*, 7(8), 1-16.

[3] Baumgardner, G. L. (2009). Polyphosphoric Acid Modified Asphalt Binders–Industry Perspective; Usage, Why, How", Paragon Technical Services, https://engineering.purdue.edu/NCSC/PPA%20Workshop/2009/index.html
(viewed 09/09/10).

[4] Burke, R. E. and Whitacre, C. H. (1939). Manufacture of Improved Asphalts, U.S.
Patent, no. 2,179,208.

[5] Changqing, F; Rulen, Y.; Ying, Z.; Jingbo, H.; Min, Z. and Xionghua, M. (2012). Combined Modification of Asphalt with Polyethylene Packaging Waste and Organophilic Montmorillonite, *Polym. Testing,* 31, 276 -281.

[6] Chen, J. S. and Huang, L. S. (2000). Developing an Aging Model to Evaluate Engineering Properties of Asphalt Paving Binders, *Mater. And Structures Const.*, 33,559-565.

[7] Daranga, C.; Clopotel, C.; Mofolasayo, A. and Bahia, H. (2009). Storage Stability and Effect of Mineral Surface on Polyphosphoric Acid (PPA) Modified Asphalt Binders. *Presented during Poster Session, 88th Annual Meeting of the Transportation Research Board; Washington, D.C.*, 2-11.

[8] Fagbote, E. O. and Olanipekun, E. O. (2011). Seasonal and Depth Effects on the Physico-chemical Parameters of the Soils of Farm Settlements with Bitumen Deposit, *Inter. Res. J. of Biotech.,* 2(9), 198-212.

[9] Feng Z. and Jianyin, Y. (2010). The Research for High-performance SBR Compound Modified Asphalt, *Const. and Build. Mater.*, 24(3), 410-418.

[10] Gupta, R. S. and Kaur, V. (2012). Characterization of Bitumen and Modified Bitumen (e-PMB) using FTIR, Thermal and SEM Techniques: International Science Congress Association, *Res .J. Chem. Sci.* 2(8), 31-36.

[11] Iliya Y. and Adam Z. (2011). Attenuated Total Reflection (ATR) Fourier Transform Infrared (FT-IR) Spectroscopy of Oxidized Polymer-Modified Bitumens, *Society for Applied Spectroscopy*, 65(7), 765-770. DOI: 10.1366/10-06217.

[12] Lamontagne, J.; Dumas, P.; Mouillet, V. and Kister, J. (2001). Comparison by Fourier Transform Infra-Red (FTIR) Spectroscopy of Different Ageing Techniques: Application to Road Bitumens, *Fuel*, 80, 483-488.

[13] Lins, V. F. C.; Araújo, M. F. A. S.; Yoshida, M. I.; Ferraz, V. P.; Andrada, D. M. and Lameiras, F. S. (2008). Photodegradation of Hot-mix Asphalt. *Fuel,* 87, 61-3254. http://dx.doi.org/10.1016/j.fuel.2008.04.039

[14] Masson, J. F. and Collins, P. (2009). FTIR Study of the Reaction of Polyphosphoric Acid and Model Bitumen Sulfur Compounds, *Energy and Fuels*, 23, 440-442.

[15] Mouillet, V.; Lamontagne, J.; Durrieu, F.; Planche, J. P. and Lapalu, L. (2008). Infrared Microscopy Investigation of

Oxidation and Phase Evolution in Bitumen Modified with Polymers, *Fuel,* 87, 80-1270. http://dx.doi.org/10.1016/j.fuel.2007.06.029

[16] Olabemiwo, O. M.; Adediran, G. O; Adekola, F. A. and Olajire A. A. (2010). Aliphatic and Polycyclic Aromatic Hydrocarbons Profiles of Photomodified Natural Bitumen of Agbabu, Southwestern, Nigeria, *Bull. Chem. Soc. Ethiop.*, 24(3), 46-466.

[17] Olabemiwo, O. M.; Akintomiwa, O. E. and Bakare, H. O. (2015). Preliminary Investigation on Modification of Agbabu Natural Bitumen with Some Polymeric Materials, *Inter. J. of Sci. and Eng. Res.*, 8(9), 1342-1349.

[18] Olabemiwo, O. M.; Akintomiwa, O. E.; GeorgeO.A., and Bakare, H. O. (2016). The performance of Agbabu Natural Bitumen Modified with Polyphosphoric Acid through Fundamental and Fourier Transform Infrared Spectroscopic Investigations, *Case Studies in Const. Mater.*,(5), 39–45.

[19] Petersen, J. C. and Harnsberger, P. M. (1998). Asphalt Aging: A Dual Oxidation Mechanism and its Interrelationships with Asphalt Composition and Oxidative Age Hardening, *In Transportation Research Record 1638*, TRB, *National Research Council, Washington, D.C*: 47–55.

[20] Rubinstein, I. and Strausz, O. P. (1979). Thermal Treatment of the Athabasca Oil Sand Bitumen and Its Component Parts, *Geo-chim. Cosmochim. Acta* 43, 1887-1893.

[21] Sa Araujo, M. A. F.; Leite L. F. M.; Pasa, V. M. D. and Lins, V. F. C. (2013). Rheological Behaviours and Thermal Behaviours of Weathering-Aged Polymer Modified Bitumen, *Brazillian J. Petrolm. and Gas,* 7(4), 155-167.

[22] Seyed, A. T. (2012). Evaluate Aging Effect of SBS Modified Bitumen, *World Academy of Sci., Eng. and Tech.,* 7, 209-212.

[23] Shulga, O., Maldonado, R., Lewandowski, L., and Romagosa, H. (2012). Application of Polyphosphoric Acid for HMA Modification. US and European Experience, *5th Eurasphalt and Eurobitume Congress, 13-15th, Istanbul*, A5EE-140.

[24] Tabatabaee, H. A; Velasquez, R. and Bahia, H. U. (2012). Predicting Low Temperature Physical Hardening in Asphalt Binders, *Const. and Build. Mater.,* 34, 9-162. http://dx.doi.org/10.1016/j.conbuildmat.2012.02.039

[25] Vernon, H. S. and Katy, T (1999). Processing for Removing Water from Heavy Crude Oil, *United State Patent. Patent no: 6,007,702.*

[26] Xiaohu, L. U.; Yohann, T. and Per, R. (2008). Aging of Bituminous Binder–Laboratory Tests and Field Data, Conference Paper, 1-12. DOI:10.