Egypt.J.Chem. **Vol. 63**, No. 6. pp. 2213 - 2233 (2020)

Egyptian Journal of Chemistry
http://ejchem.journals.ekb.eg/

Improving The Aging Effect of Bitumen and SBS Modified Bitumen by Using Newly Prepared Antioxidants

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THERMAL oxidative aging of bitumen has a bad effect on the durability of bitumen binder. We aim in this research to reduce the thermal oxidative aging of bitumen by preparing two compounds namely (R-OCH_3=AO_1) and (R-NO_2=AO_2) and examined as antioxidants. These compounds characterized via the conventional spectral tools of analysis (FTIR and ^{1}H-NMR). They mixed with local bitumen (60/70) separately at different concentrations ratios (0.25, 0.5 and 1%) then aged via TFOT at 170°C for 5 hours. The effect of them evaluated based on the changes in FTIR, total acid number (TAN) and the physical properties of bitumen before and after the thermal oxidation. The results showed that 0.5, 1% of AO_1 antioxidant gave the best results of modification of bitumen. After the samples modified with these two concentration ratios of antioxidant AO_1, they mixed with 3% Styrene Butadiene Styrene (SBS) polymer then aged via TFOT at 170˚C for 5 hours. The effect of the antioxidant in reducing the aging of the SBS modified bitumen (SBSMB) was evaluated through the changes in FTIR, TAN and the physical properties of bitumen before and after the thermal oxidation. The results illustrated that the best modification of SBSMB was at 1% (AO_1).

Keywords: Bitumen, Oxidative Aging, Antioxidants, Physical Properties and Total Acid Number.

Introduction

Thermal oxidative aging of bitumen is an irreversible chemical reaction between bitumen and the atmospheric oxygen **[1]**. Oxidation of bitumen can occur rapidly during mixing with hot aggregates, transportation, laying and compaction and /or when bitumen is modified with polymers at elevated temperatures above 170˚C and high sheer rate for a long time (2-4 hours) **[2, 3]**. While it can be oxidized also slowly during service life **[4]**.

Aging significantly changes both physical and chemical properties of bitumen. Physical properties such as viscosity, softening point, penetration and ductility are changed to some extend after aging **[5-7]**.

When bitumen aged at elevated temperatures (170˚C), the C=C bond is broken leading to the formation of free radicals which combined with the atmospheric oxygen to form the carbonyl groups which result in the change in the chemical properties of bitumen **[8, 9]**. The addition of antioxidants act as scaventures of the free radicals and oxygen leading to retardation of the thermal oxidation of bitumen **[10, 11]**. These changes in the physical and chemical structure make the bitumen binder more harder and more brittle which led to reducing the durability and the life time of bitumen pavement **[12, 13].**

Styrene Butadiene Styrene triblock copolymer (SBS) is mixed with bitumen to improve its stiffness at low temperature and reduce the

*Corresponding author: ah_samy2012@yahoo.com
Received 24/10/2019; Accepted 14/11/2019
DOI: 10.21608/ejchem.2019.18500.2151

rutting at elevated temperatures **[14, 15].** When bitumen is mixed with SBS at high temperature above 170˚C and high shear rate for 4 hours, both bitumen and SBS were aged. The aging process of SBS modified bitumen at elevated temperatures includes the oxidation of the base bitumen and the oxidation of the degraded SBS chain **[16, 17].**

Many researches have been carried out to study the effect of addition small quantities of antioxidants to the base bitumen to retard the aging of the bitumen and SBS modified bitumen. The changes in the physical properties, total acid number and FTIR are the most common method are the most common methods used by many investigators to study the net changes in the bitumen and SBS modified bitumen after aging **[1, 18-20].**

These researchers studied the effect of the antioxidants on reducing the thermal oxidative aging of SBSMB. Ouyang C., et al., studied the effect of zinc dialkyldithiophosphate (ZDDP) and zinc dibutyl dithiocarbamate (ZDBC) oil **[21].** Feng Z., et al., studied the impacts of additives (bumetrizole, octabenzone, and tinuvin770) **[22].** Hoda A. M., et al., studied the effect of some Thiazolidinones as antioxidants **[23]**. Kuang D., et al., studied the effect of Irganox1010 **[24].** Zhang D., et al., examined the influence of Nano- zinc oxide (Nano-ZnO) and organic extended vermiculite (OEVMT) **[25].** Yuan, J., et al., studied the effect of naphthenic oil as antioxidants to retard the thermal oxidative aging of SBS modified bitumen **[26].** All the results showed that there is enhancement in the properties of the SBSMB after addition of these antioxidants.

In this work, we aim to reduce the thermal oxidative aging of bitumen and SBS modified bitumen by addition of two newly prepared compounds and studying their antioxidation ability to retarde this thermal oxidative aging.

Experimental Techniques and Materials

Materials

Bitumen: local bitumen of penetration grade 60/70 produced by Alexandria Petroleum Company. Its physical properties are inserted in table (1) and the chemical compounds used and their sources are listed in table (2).

Methods

Preparation of the antioxidants

Diazotization of different amines

In ice path, 0.05 mol of aromatic amine dissolved in 20ml dist. water and 20ml Conc. HCL till making clear solution then 0.05 mol of sodium nitrite ($NaNO_2$) was added drop wise to this solution to obtain the diazonium salt.

Coupling with Guaiacol

In ice path, 0.05 mol of Guaiacol is dissolved in 0.05 mol of NaOH then this solution was added to the first solution of diazonium salt then stirring further 20 min and the product was acidified by acetic acid then washed

Preparation of the aged bitumen (AB)

The base bitumen was heated via the thin film oven test (TFOT) at 170°C for five hours, this temperature is the maximum temperature achieved during the mixing of bitumen with polymer.

Preparation of aged antioxidant modified bitumen (AAMB)

The base bitumen was heated to 140°C and our prepared antioxidants were added separately with different concentrations (0.25, 0.5, and 1 %) by wt. of the base bitumen while stirring then the blends exposed to the thermal oxidation via TFOT at 170°C for 5 hours .

TABLE 1. The physical properties of the base bitumen.

Properties	Value
Penetration at 25°C,100g,5 seconds and 0.1 mm	61
Kinematic viscosity at 135°C	340
Flash point °C ,(Cleveland open cup)	+250
Softening point °C ,(ring & ball)	48
Solubility in Trichloroethylene	99.8%
Ductility at 25°C	+100

TABLE 2. Chemicals used and their sources,

Chemical Compound	Source
Styrene Butadiene Styrene (SBS)	Merck
P-Methoxy Aniline	Aldrich
P- Nitro Aniline	Aldrich
Guaiacol (Methoxy Phenol)	Merck
Sodium Nitrite ($NaNO_2$)	Aldrich
Hydrochloric Acid (HCL)	Aldrich
Acetic Acid (CH_3COOH)	Aldrich
Acetone	Aldrich
Sodium Hydroxide (NaOH)	Merck

with dist. water and recently recrystallized from acetic acid. The structure of the prepared antioxidants is confirmed through FTIR and ^{1}H-NMR (type Varian 300 MHz) with the TMS as internal standard zero compound .

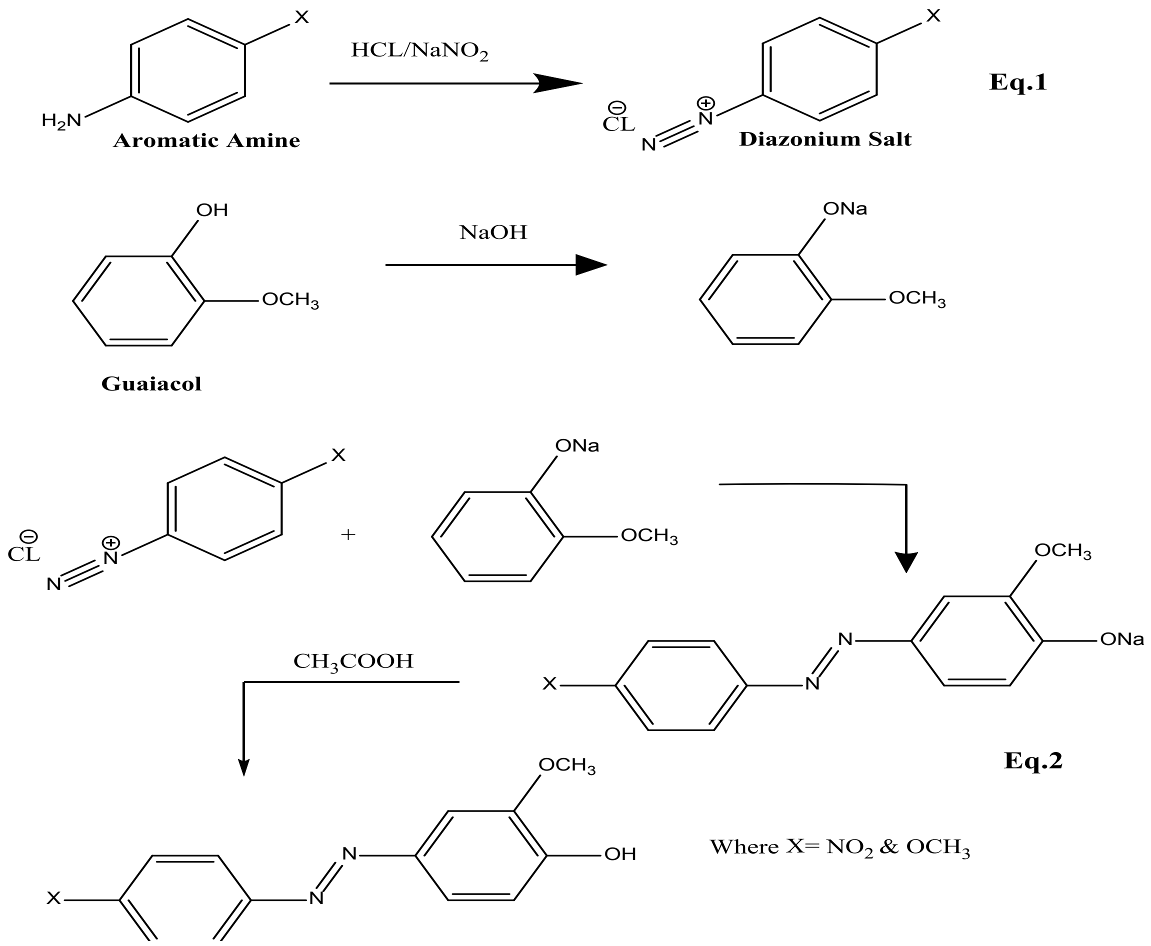


Fig. 1. Synthesis of the antioxidants.

Preparation of Aged Polymer Modified Bitumen (APMB)

The base bitumen was heated in air in oil path to 140°C Then 3% SBS by wt. of bitumen was added while stirring then the temperature was raised to 170°C and the stirring was continued for four hours then the blend was aged at 170°C via the thin film oven test (TFOT) for five hours.

Preparation of the aged antioxidant / polymer modified bitumen (AAPMB)

The best results in modification of bitumen properties within the thermal oxidation were at [AO_1 (0.5%) and AO_1 (1%)], so the base bitumen heated to 140°C then the selected antioxidants added separately to the heated bitumen with stirring for 20 min. After that, the temperature of this blend raised to 170°C and (3% SBS polymer by weight of base bitumen) added with stirring for four hours. Then this blend was aged through the thin film oven Test (TFOT) at 170°C for five hours. Finally, we have 12 samples under test to be evaluated.

Evaluation of the blends

The abbreviations of the bitumen blends showed in table (3) and the properties of the base, aged, aged antioxidant, aged antioxidant /polymer-modified bitumen were examined according to standard test methods as following:

Physical properties

Kinematic viscosity, Ring and ball test (softening point temperature), Penetration test and Ductility test (ASTM D2170-76, D2398-76, D5-73 and D113-76 respectively).

Fourier Transform Infrared Spectroscopy (FT-IR)

FTIR was used to know the functional characteristics of the base bitumen, aged bitumen, polymer modified bitumen and antioxidant polymer modified bitumen. To obtain detailed information about the molecular structure of any sample, the IR transmission spectroscopic investigation was carried out at room temperature on FT-IR, JASCO, Nicolet IS-10 (made in Japan) spectrometer using K-Br disc method **[27]**.

Total acid number

According to ASTM D-664, the total acid number (TAN) is a measurement of acidity that is determined by the amount of potassium hydroxide in milligrams that is needed to neutralize the acids in one gram of oil. It is an important quality measurement of bitumen. TAN value can be obtained by the Potentiometric titration at which the sample is normally dissolved in toluene and isopropanol and titrated with alcoholic potassium hydroxide (if sample is acidic).

TABLE 3. Abbreviation of the bitumen blends according to the type of antioxidant and its concentration.

Type of antioxidant	Conc. Ratio of antioxidant	Abbreviations of the blends after addition of antioxidants	Abbreviations of the blends after addition of antioxidants and SBS
AO_1	0.25%	Bit. /AO_1 (0.25%)	-
	0.5%	Bit. /AO_1 (0.5%)	Bit. /AO_1 /SBS (0.5%)
	1%	Bit. /AO_1 (1%)	Bit. /AO_1 /SBS (1%)
AO_2	0.25%	Bit. /AO_2 (0.25%)	-
	0.5%	Bit. /AO_2 (0.5%)	-
	1%	Bit. /AO_2 (1%)	-

Results and Discussion

Characterization of the prepared antioxidants

FTIR of the prepared antioxidants

Fig. (2) shows peak at 2837 & 2950 cm^{-1} indicated to CH aliphatic, peak at 3084 cm^{-1} indicates to CH aromatic , peak at 1209 cm^{-1} agree with C-O-C. We can also see peak at 1595 cm^{-1} indicated to C=C, N=N which identified with peak at 1443 cm^{-1} and peak at 3500 cm^{-1} corresponds to OH group.

Fig. (3) shows peak frequency 2885 cm^{-1} that indicates to C-H aliphatic bond, peak at 3078 cm^{-1} corresponds to C-H aromatic bond, peak at 1109 cm^{-1} shows the occurrence of C-O-C. As well as peak at 1596 cm^{-1} refers to C=C, peak at 1430 cm^{-1} indicated to N=N, peak at 1545 cm^{-1} indicated to C-NO_2 and peak at 3375 cm^{-1} agree with OH group.

[1]H-NMR of the antioxidants

The chemical shift of the prepared antioxidant compounds are given in tables (4, 5) and Figures (4, 5):

Evaluation of the prepared blends

The properties of the base, aged, aged antioxidant, aged antioxidant /polymer-modified bitumen were examined according to standard test methods as follows:

Physical properties

By measuring of their Kinematic Viscosity, Softening point and Penetration.

The physical properties of base bitumen and antioxidant-modified bitumen are listed in table (6)

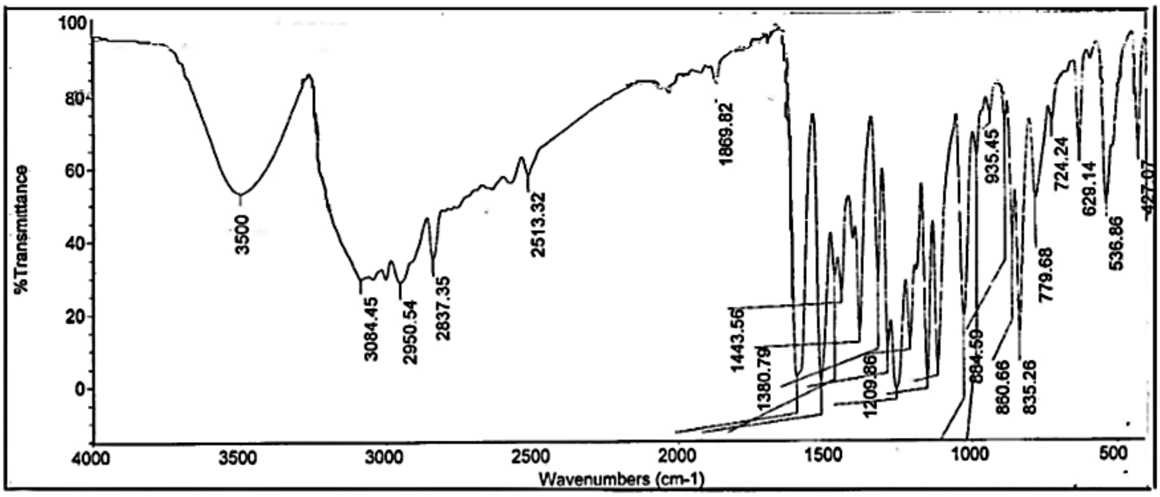


Fig. 2. FTIR of AO_1 antioxidant.

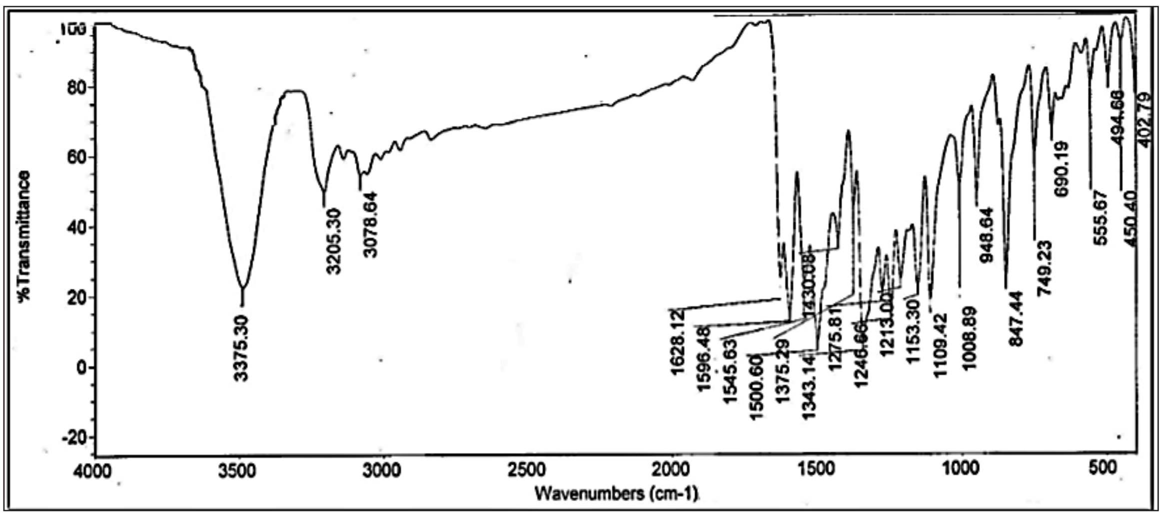
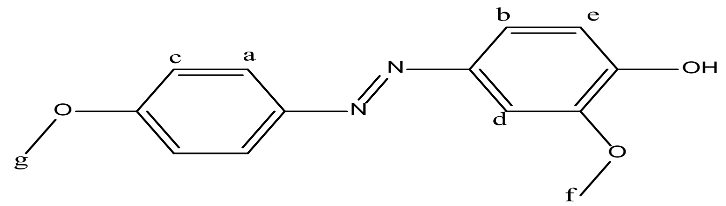


Fig. 3. FTIR of AO_2 antioxidant.

TABLE 4. Chemical shifts of AO_1 antioxidant.



H+ Type	a (d)	b (d)	c (d/d)	d (d)	e (d)	f (s)	g (s)	OH proton (s)
Chemical shift	7.783	7.651	7.522	7.354	7.075	4.002	2.449	9.432

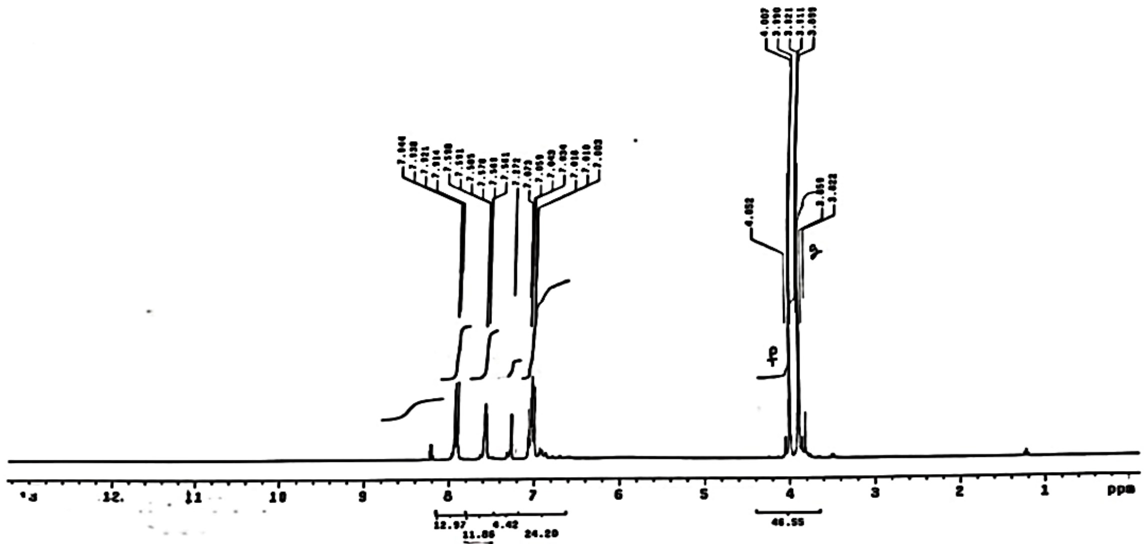
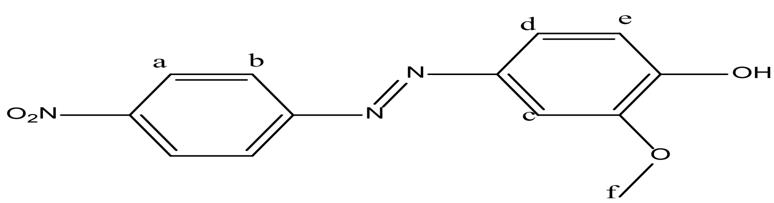


Fig.4.The [1]H-NMR of AO_1 antioxidant .

TABLE 5. Chemical shifts of AO_2 antioxidant.



H+ Type	a (d)	b (d)	c (d/d)	d (d)	e (d)	f (s)	OH proton (s)
Chemical shift	8.376	8.180	7.545	7.273	7.029	3.988	9.467

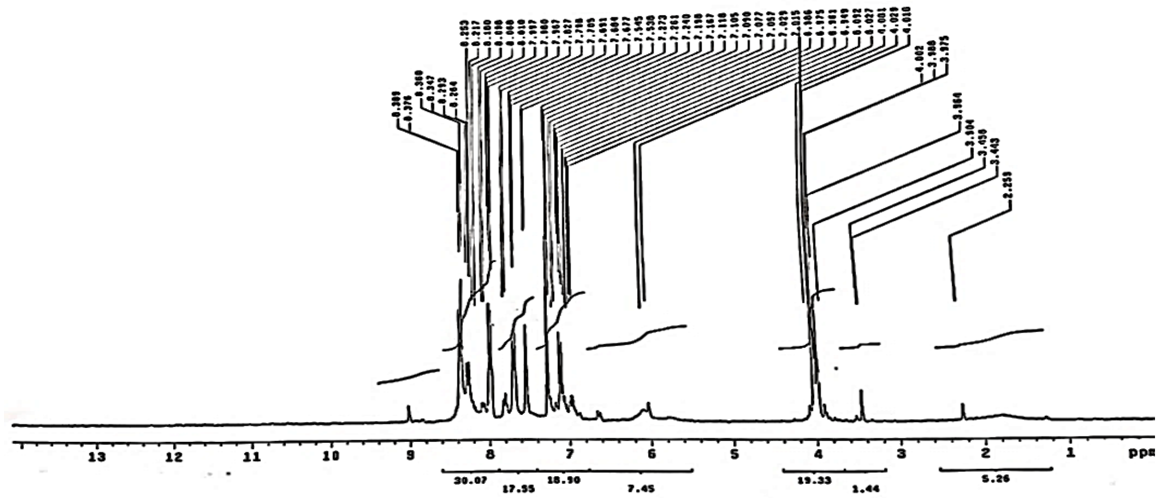


Fig. 5. The ^{1}H-NMR of AO_2 antioxidant.

TABLE 6. The physical properties of base bitumen and antioxidant modified bitumen.

Treatment	Results of the physical properties			Change Percent in the physical properties after addition of AOs after TFOT		
	VIS.	SOFT.	PEN.	VIS. %	SOFT. %	PEN. %
Base bitumen	**340**	**48**	**61**	-	-	-
Base bitumen after TFOT	**464**	**52**	**36**	+ 36.47%	+ 8.33%	- 41%
Bit. /R-OCH_3 (0.25%)	379	53	39	- 18 %	- 1.92 %	+ 8.33 %
Bit. /R-OCH_3 (0.5%)	367	52	45	- 21 %	- 3.84 %	+ 25 %
Bit. /R-OCH_3 (1%)	372	52	41	- 19.8 %	ZERO	+ 13.8 %
Bit. /R-NO_2 (0.25%)	483	54	29	+ 4.09 %	+ 3.84 %	- 19.4 %
Bit. /R-NO_2 (0.5%)	474	53	33	+ 2.15 %	+ 1.92 %	- 8.3 %
Bit. /R-NO_2 (1%)	490	55	26	+ 5.6 %	+ 5.77 %	- 27.7 %

Kinematic Viscosity

From table (6) and figures (6, 7), it can be noted that: the viscosity value of the base bitumen increased by 36.47% under the short-term aging while the viscosity of bitumen decreased by 18%, 21%and 19.8% when modified with AO_1 antioxidants with the three different concentration ratios (0.25%, 0.5% &1%) respectively comparing to the viscosity of base bitumen after aging. These antioxidants made the viscosity of AOMB near to that of the base bitumen. This decrease in viscosity of bitumen when modified with this antioxidant may be due to the electron donating function group present in this antioxidant which made localization of the lone pair of electrons on N=N atoms present in the antioxidant compound. These lone pair of electrons are responsible for capture of oxygen and prevent it from reaching to bitumen. The increase of the antioxidation ability of these compounds decrease the oxidation and hence decrease the viscosity of bitumen modified with these antioxidants. When AO_2 antioxidant added to the base bitumen with the three different concentration ratios (0.25%, 0.5% &1%), the viscosity of the AOMB after aging increased by 4.09%, 2.15%, 5.6% respectively comparing to the viscosity of the base bitumen after aging. This increase in viscosity after aging of bitumen when modified with this antioxidant may be due to the electron withdrawing function group present in this antioxidant which made delocalization of the lone pair of electrons on N=N atoms present in the antioxidant compound. However, when the delocalization of these lone pairs of electrons occurs under the effect of the electron with drawing function group, the ability of the antioxidant to capture oxygen decreased due to the –I effect of NO_2 group. The decreasing of the antioxidation ability of these compounds made remain portions of these antioxidants act as fillers, which led to increasing the viscosity of bitumen modified with these antioxidants.

Softening point

The thermal oxidation of bitumen also led to increasing the softening point of it. Table (6) and Figs. (8, 9) illustrate the softening point of the base bitumen before and after TFOT and that of the antioxidants modified bitumen after TFOT only. It can be noted that the softening point of the aged bitumen increased by 8.33% comparing to the base bitumen. There was a slight increase in the softening point for all examined antioxidants treatments after TFOT comparing to the base bitumen after aging. The changes in the softening point resulted from the addition of different antioxidants treatments after TFOT comparing to the aged bitumen can be ranged from 5.77 % for (1%) AO_2, which represent the highest percent of change in softening point to – 3.84% for (0.5%) AO_1, which represent the lowest percent of change in the softening point comparing to that of the aged bitumen, which near to the softening point that of the base bitumen. The lower the change percent of the softening point, the better the antioxidant used.

Penetration

Not only the viscosity and softening point of bitumen that were changed upon the thermal oxidative aging but also the penetration degree. Tab. (6) and Figs. (10, 11) illustrate the penetration of the base bitumen before and after TFOT and the penetration of the antioxidants modified bitumen after TFOT only. It can be noted that the penetration of the aged bitumen decreased by 41% comparing to the base bitumen. As mentioned in viscosity section, when R-NO_2 antioxidant added to bitumen with different concentration ratios and due to the presence of the electron withdrawing groups in this compounds this led the remain portions of these compounds to act as fillers which result in decreasing the penetration. The penetration of bitumen increased by 8.33%, 25% and 13.8% when modified with AO_1 antioxidant with the three different concentration ratios (0.25%, 0.5% &1%) respectively comparing to the viscosity of base bitumen after aging. This increase in penetration is due to the reason mentioned before in the viscosity section that is the presence of the electron donating function groups in these compounds. The highest increase in penetration value reached to 25% when the antioxidant R-OCH_3 added to bitumen with concentration ratio 0.5%. The higher the increase in penetration value, the better the antioxidant used.

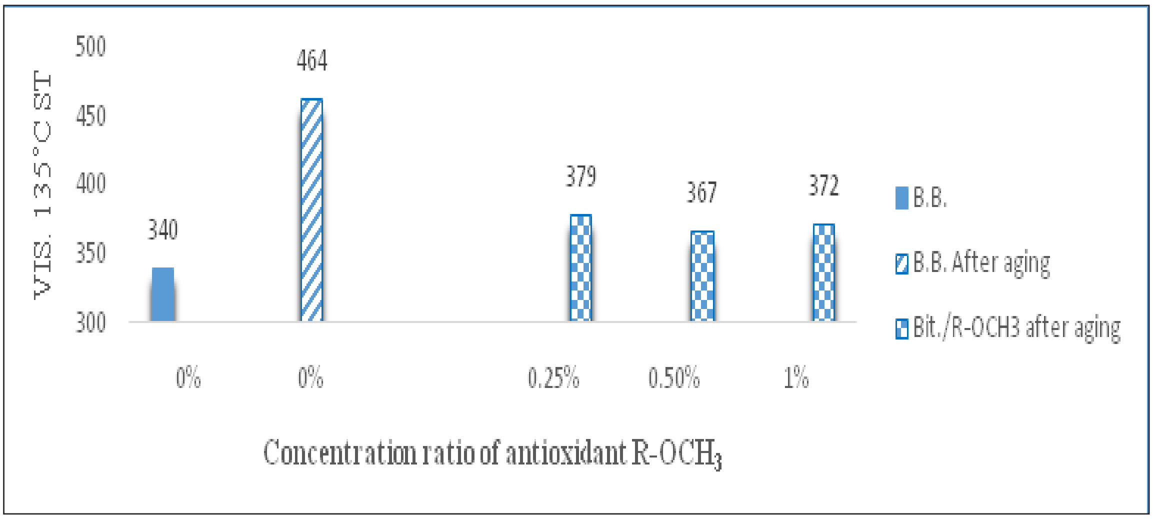


Fig. 6. Viscosity of bitumen at different concentration ratios of AO_1

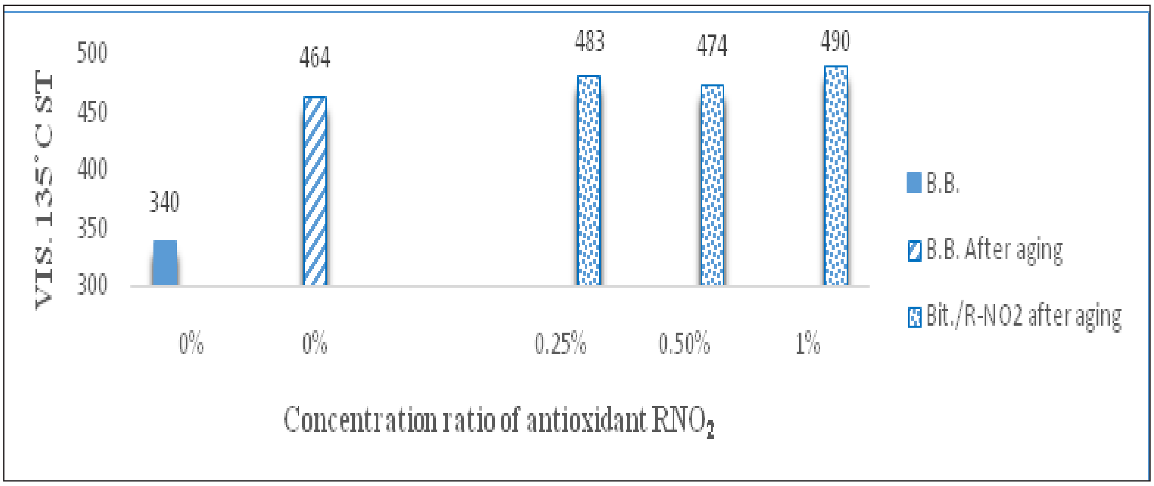


Fig. 7. Viscosity of bitumen at different concentration ratios of AO_2.

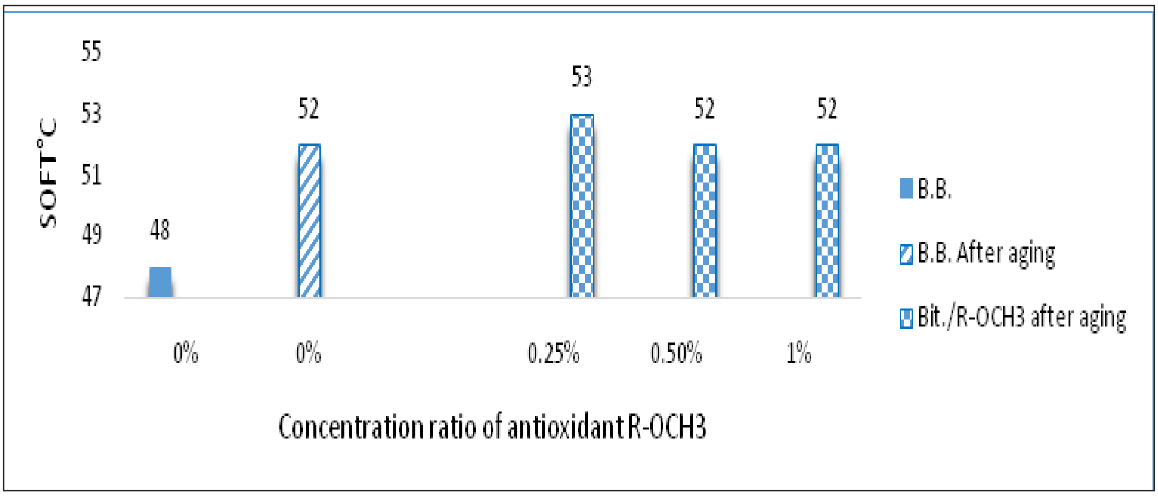


Fig.8. Softening point of bitumen at different concentration ratios of AO_1.

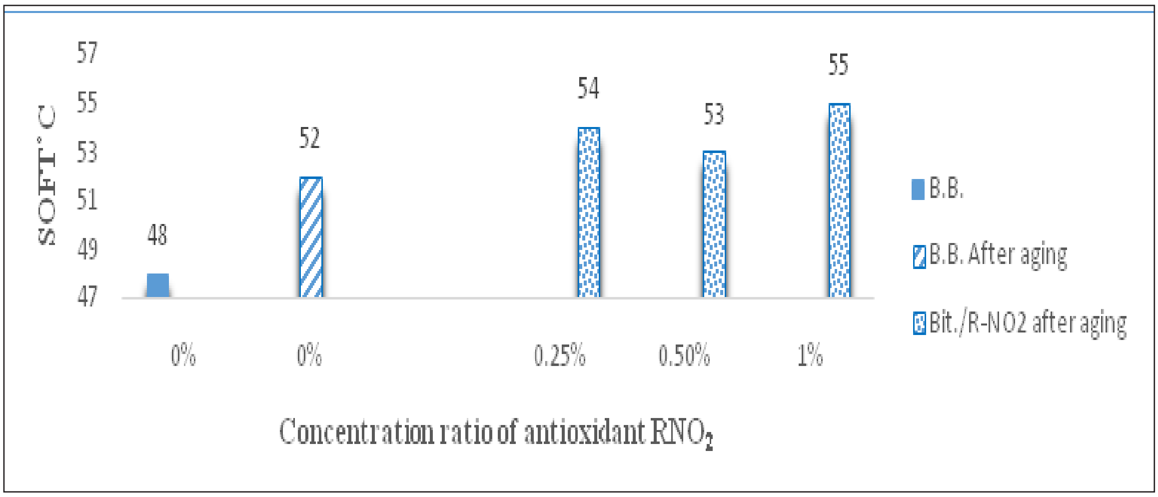


Fig. 9. Softening point of bitumen at different concentration ratios of AO_2.

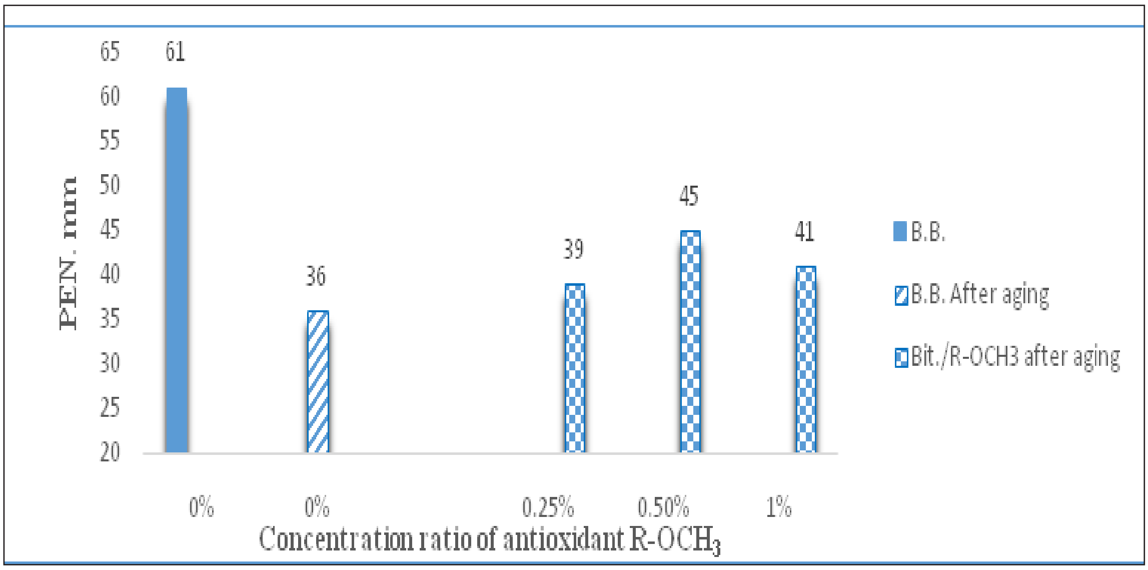


Fig. 10. Penetration of bitumen at different concentration ratios of AO_1.

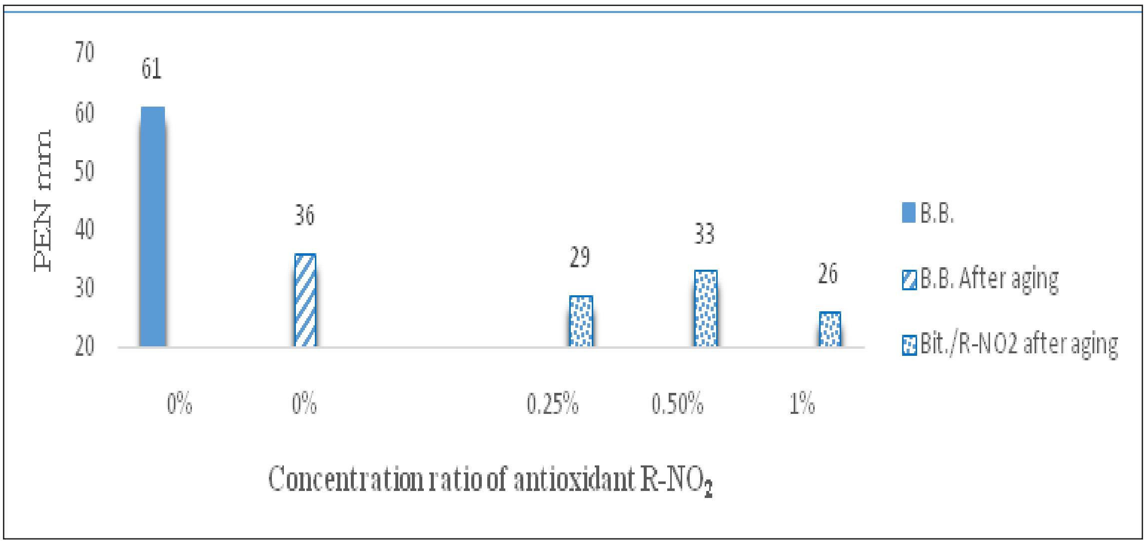


Fig. 11. Penetration of bitumen at different concentration ratios of AO_2.

TABLE 7. The physical properties of blends after addition of SBS.

Sample	VIS.	SOFT.	PEN.	DUC.
Bit./ SBS Before TFOT	790	85	14	5
Bit./ SBS After TFOT	762	70	40	44
Bit./AO_1 (0.5%)/SBS After TFOT	794	72	31	30
Bit./AO_1 (1%)/SBS After TFOT	806	79	29	22

From table (7) and figures (12-15) it can be noted that When 3% SBS was introduced to the base bitumen at 170˚C while stirring for four hours, the viscosity and softening point were increased sharply while the penetration and ductility were decreased. This may be due to the absorption of the most light weight fractions of bitumen by SBS **[28],** and formation of network structure with bitumen at 170˚C. When SBSMB was aged via TFOT at 170˚C for five hours, the viscosity and softening point were decreased by 3.54% and 17.6% respectively while penetration and ductility are increased by 185% and 780% respectively comparing to those of SBS modified bitumen before TFOT. This may be due to the degradation of SBS network structure and reducing the interaction between bitumen and SBS polymer, which led to realizing of the light fractions absorbed before which responsible for bitumen to be soft.

When the selected antioxidant AO_1 with different concentration ratios (0.5% & 1%) were added separately to the base bitumen before mixing with SBS polymer then aged via TFOT at 170˚C for 5 hours, the viscosity and softening point re-increased and became higher than those without antioxidants. The increase was by 4.2% and 5.77% for viscosity and by 2.85% and 8.57% for softening point respectively while penetration and ductility were decreased by 22.5% and 27.5% for penetration and by 32% and 50% for ductility respectively comparing to the aged SBSMB.

These changes in the physical properties after addition of antioxidants were due to decreasing the oxidation of bitumen and in the same time decreasing the degradation of SBS in SBSMB blend. The higher increase in viscosity, increase in softening point, decrease in penetration and decrease in ductility, the bitter the antioxidant used. The best antioxidant that give the best results when mixed with SBS and bitumen was AO_1 with concentration ratio 1%.

This can be confirmed by FTIR and T.A.N. data.

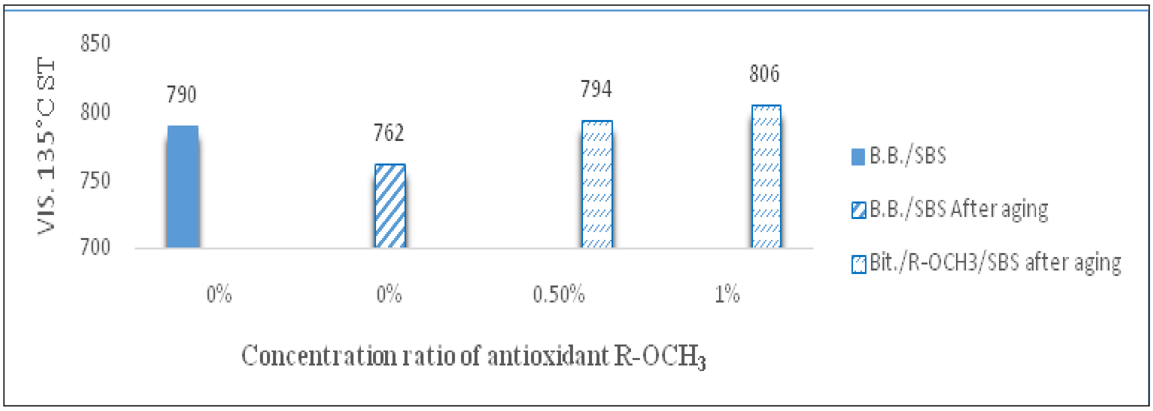


Fig. 12. Viscosity of SBSMB at different concentration ratios of AO1 .

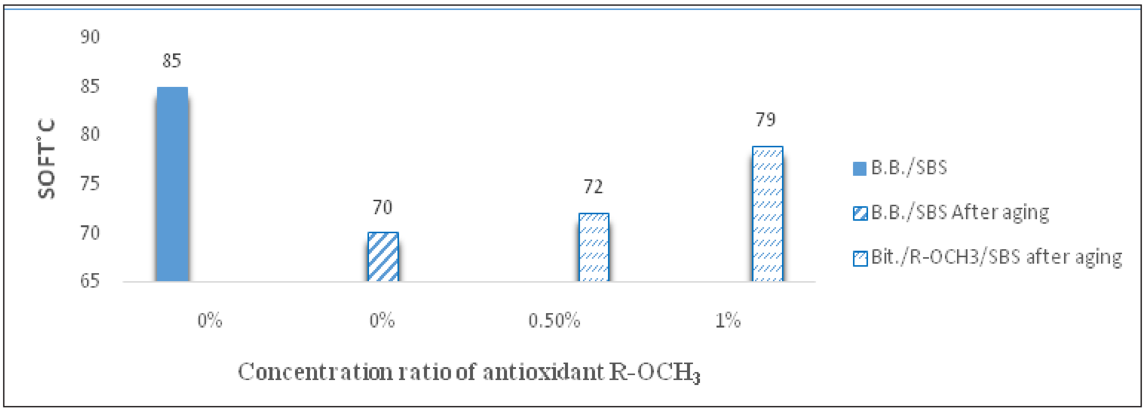


Fig. 13. Softening point of SBSMB at different concentration ratios of AO_1 .

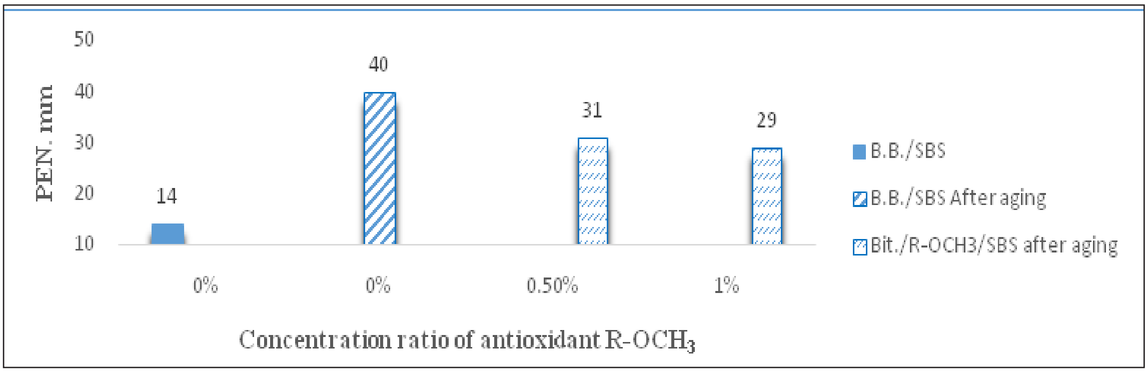


Fig. 14. Penetration of SBSMB at different concentration ratios of AO_1.

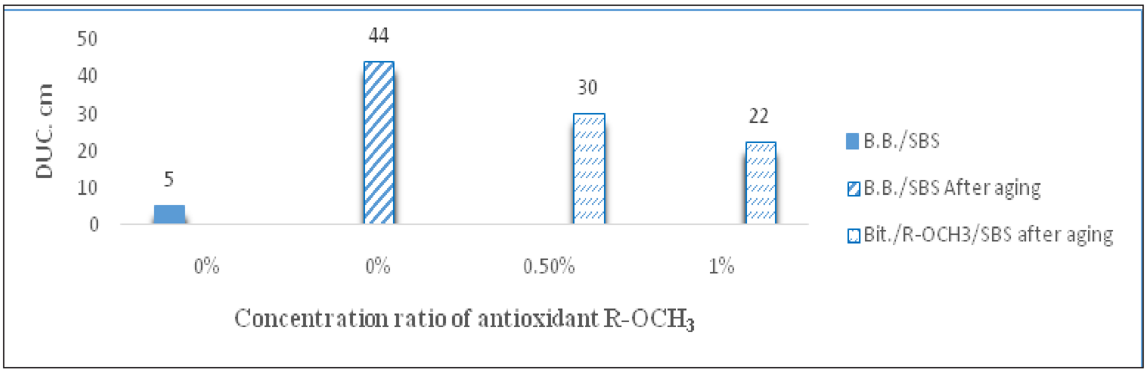


Fig. 15. Ductility of SBSMB at different concentration ratios of AO_1.

FTIR analysis of the prepared blends

Comparing to Figure (16) which represent the FT-IR of the base bitumen, Figure (17) which represents the FT-IR of the aged bitumen shows the increasing the intensity of a peak at 1749 cm^{-1} which identifies the increasing of formation of carbonyl group C=O bond that may be occurred due to the thermal oxidation of bitumen. From figures (18-20), it can be noted that the addition of the antioxidants made retardation in the thermal oxidation of bitumen by reducing the formation of the carbonyl groups due to the antioxidation ability of AO_1 antioxidant. According to Figures (21-23), the major band at frequency 1704, 1700 and 1704 cm^{-1} that corresponds to the presence of the carbonyl group, which formed when the blends Bit. /AO_2 at different concentration ratios of AO_2 (0.25%, 0.5% and 1%) were aged via TFOT respectively. This may confirm the results obtained from the measurements of the physical properties, which showed an increase in the viscosity and softening point and a decrease in penetration that were explained due to the small antioxidation effect of AO_2 antioxidant. The best antioxidant is AO_1 at concentration ratio 0.5%.

Figure (24) showed peak at 966 cm^{-1} which corresponds to C=C in butadiene and peak at 723 cm^{-1} which indicate to the presence of styrene. There is a small peak present in figure (24) at 1723 cm^{-1} which corresponds to the C=O bond. This peak is small comparing to the peak appeared for base bitumen in Figure (16) and this is due to the addition of SBS polymer. The SBS polymer made absorption of the light fractions, which are more susceptible to oxidation and hence decrease the thermal oxidation of these light fractions.

When bit. /SBS blend was aged via TFOT, the blend is oxidized and the C=O bond formation increased due to the C=C bond in the butadiene fraction of SBS polymer was declined with aging and this can be noticed in figure (25).

FT-IR represented in Figs. (26, 27) of Bit. / SBS blends after aging in presence of the best concentration ratios of AO_1 showed that there is an enhancement in the oxidation retardation of Bit. /SBS blends. This is may be due to the double effect of the antioxidants, which decrease the thermal oxidation of bitumen and the degradation of SBS polymer. The best modification of SBSMB was at 1% of AO_1.

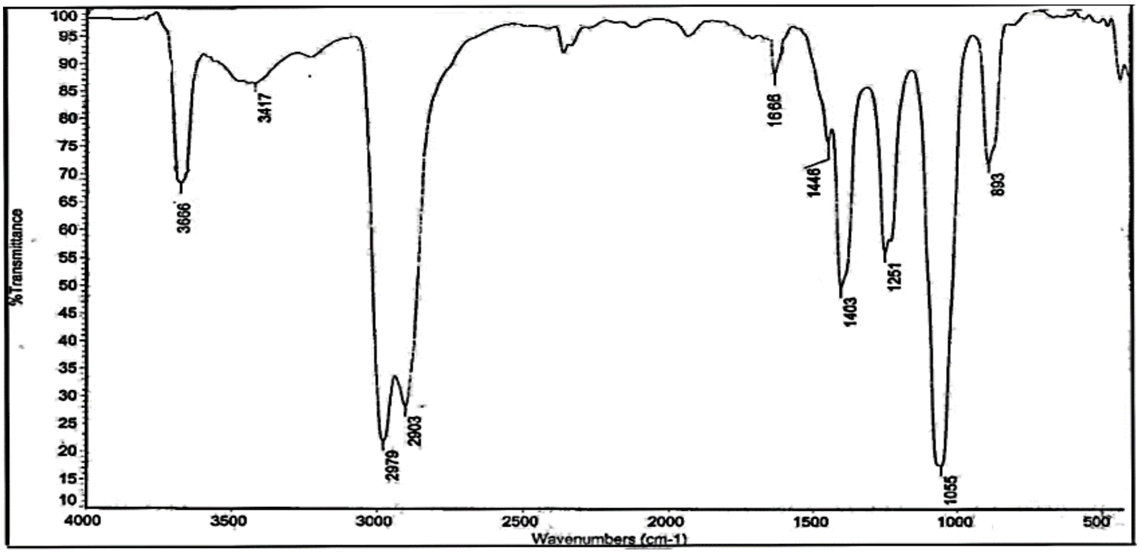


Fig. 16, FTIR of the base bitumen.

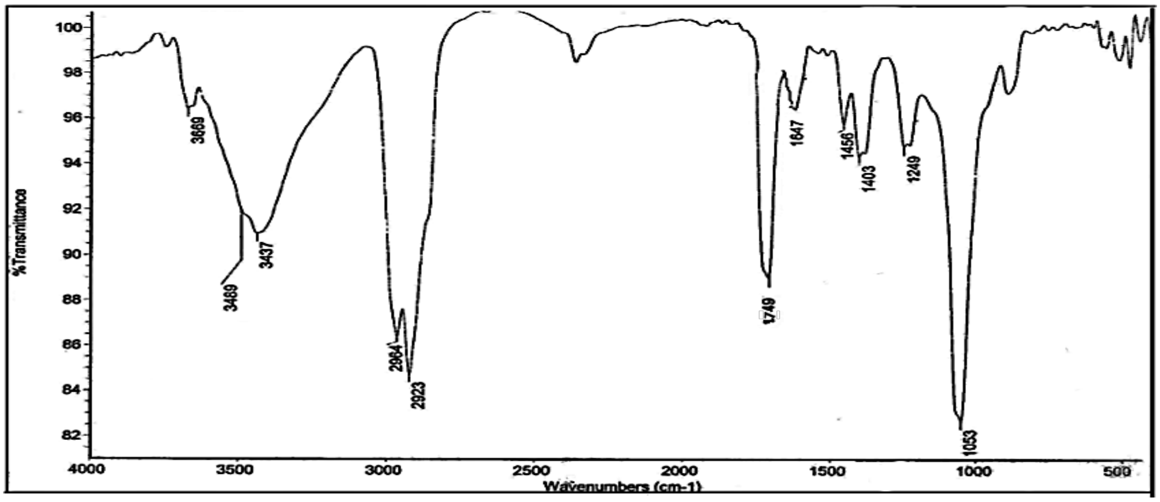


Fig. 17. FT-IR of the base bitumen after TFOT.

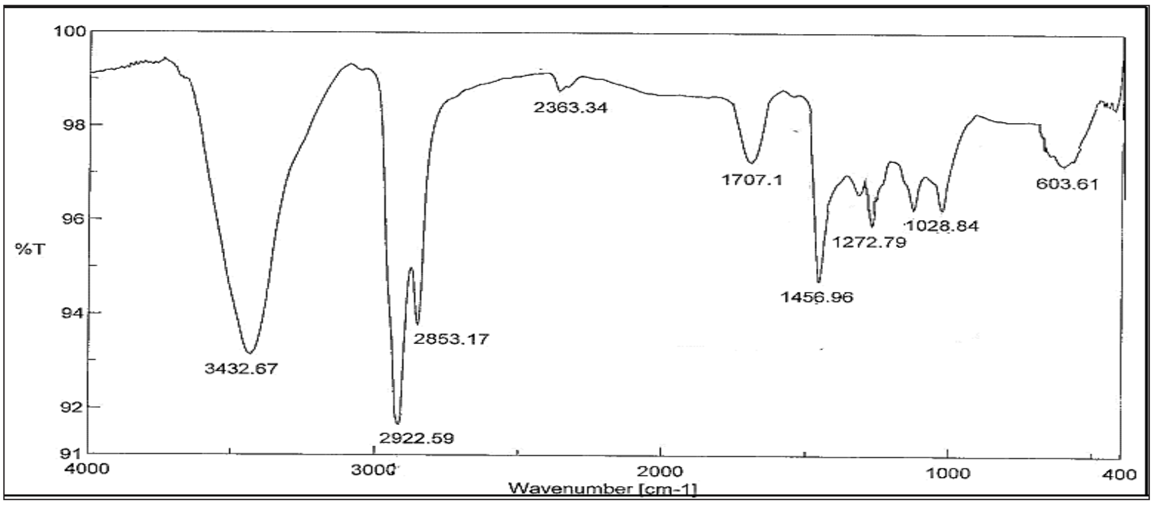


Fig.18. Effect of (0.25%) AO_1 on the thermal oxidation of bitumen.

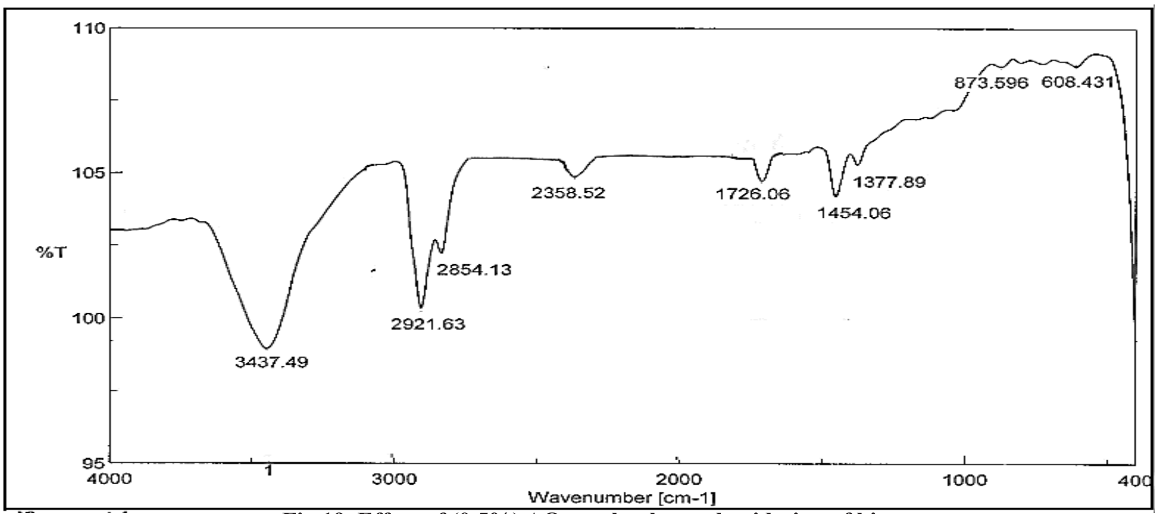


Fig.19. Effect of (0.5%) AO_1 on the thermal oxidation of bitumen.

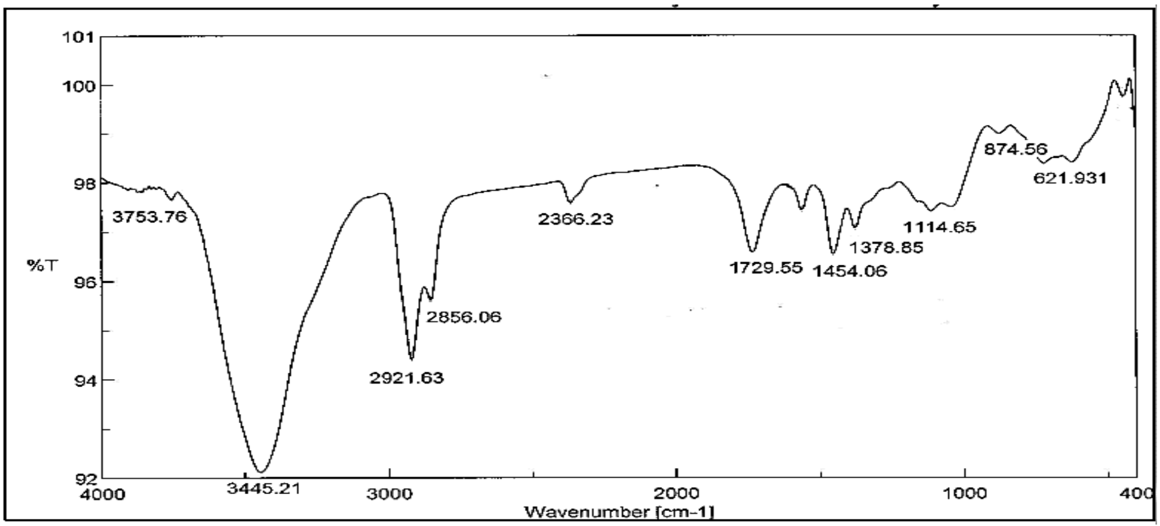


Fig. 20.Effect of (1%) AO_1 on the thermal oxidation of bitumen.

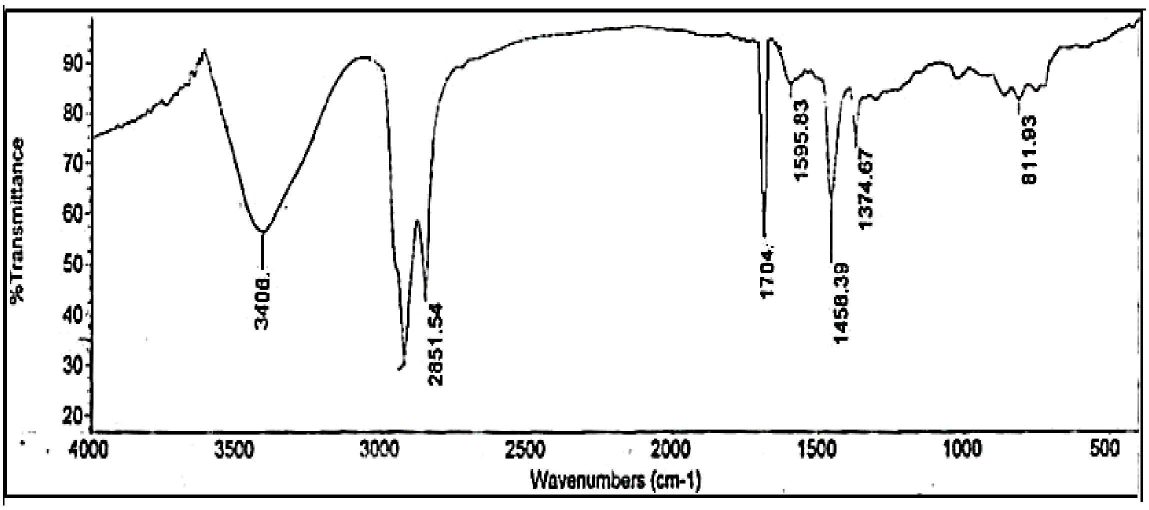


Fig.21. Effect of (0.25%) AO_2 on the thermal oxidation of bitumen.

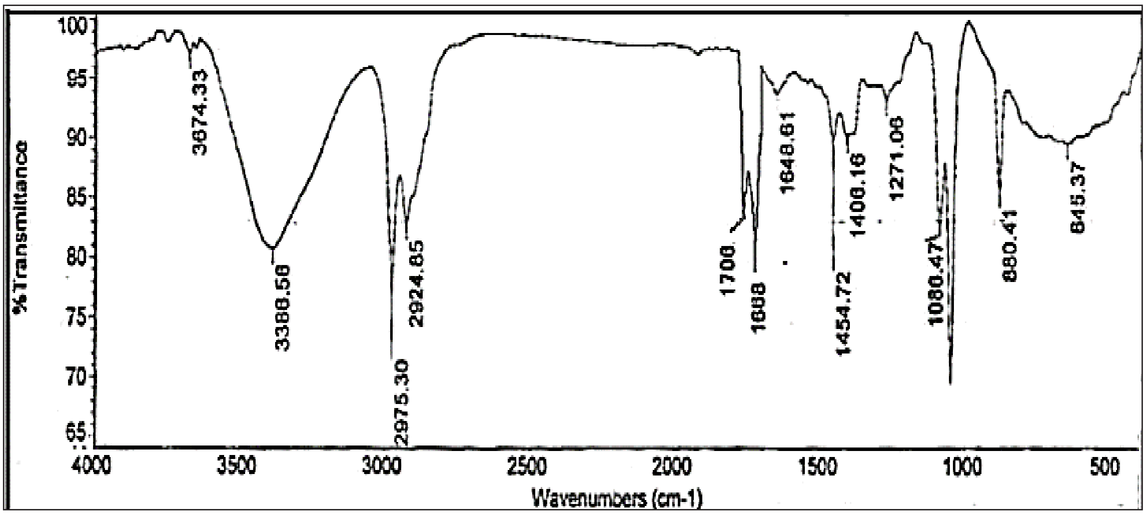


Fig. 22. Effect of (0.5%) AO_2 on the thermal oxidation of bitumen.

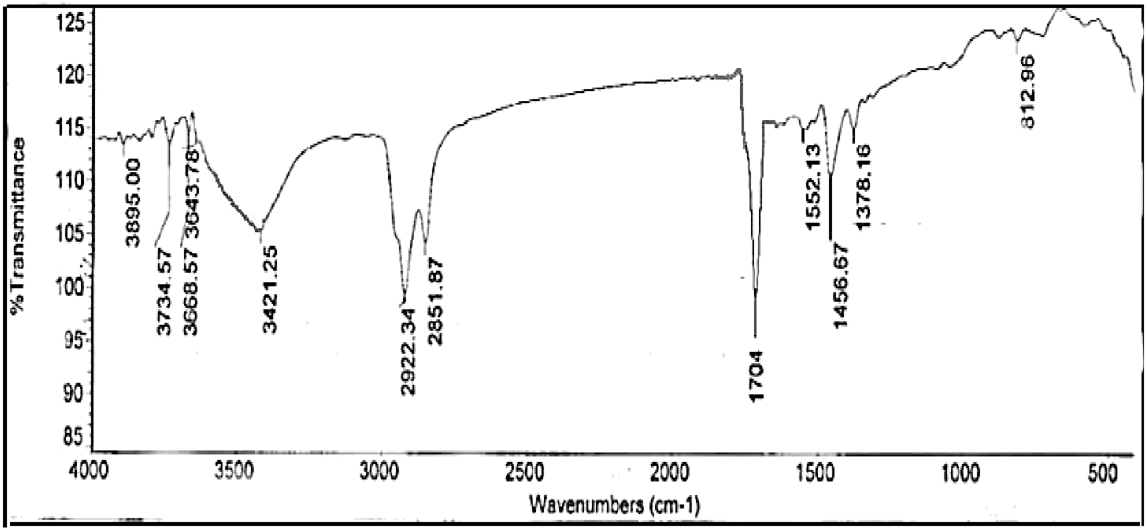


Fig. 23. Effect of (1%) AO_2 on the thermal oxidation of bitumen.

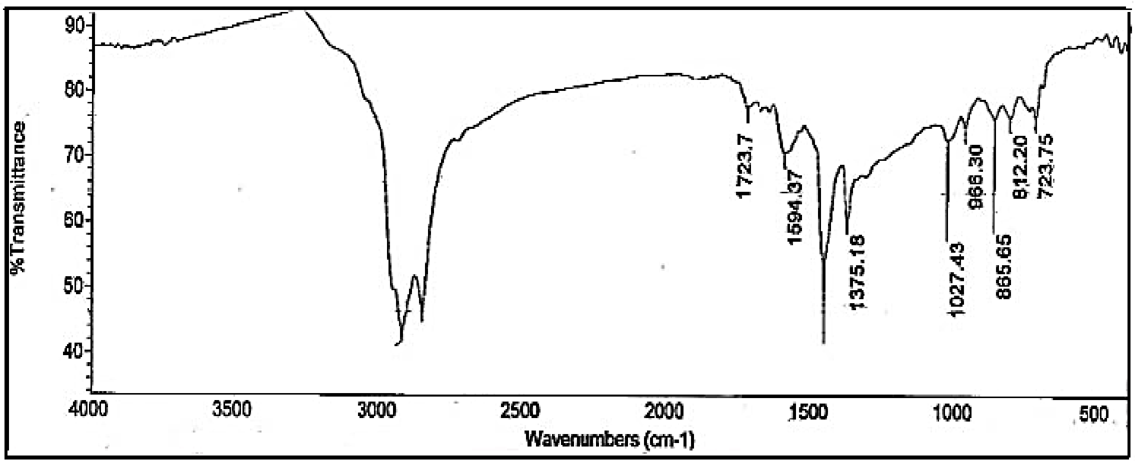


Fig. 24. FT-IR of Bit. /SBS blend before TFOT.

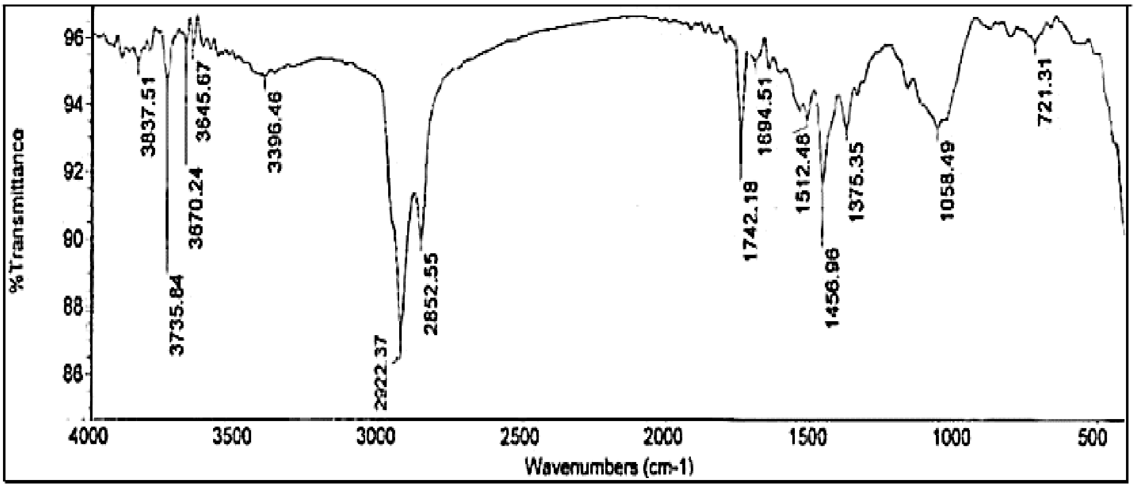


Fig. 25. FT-IR of Bit. /SBS blend after TFOT.

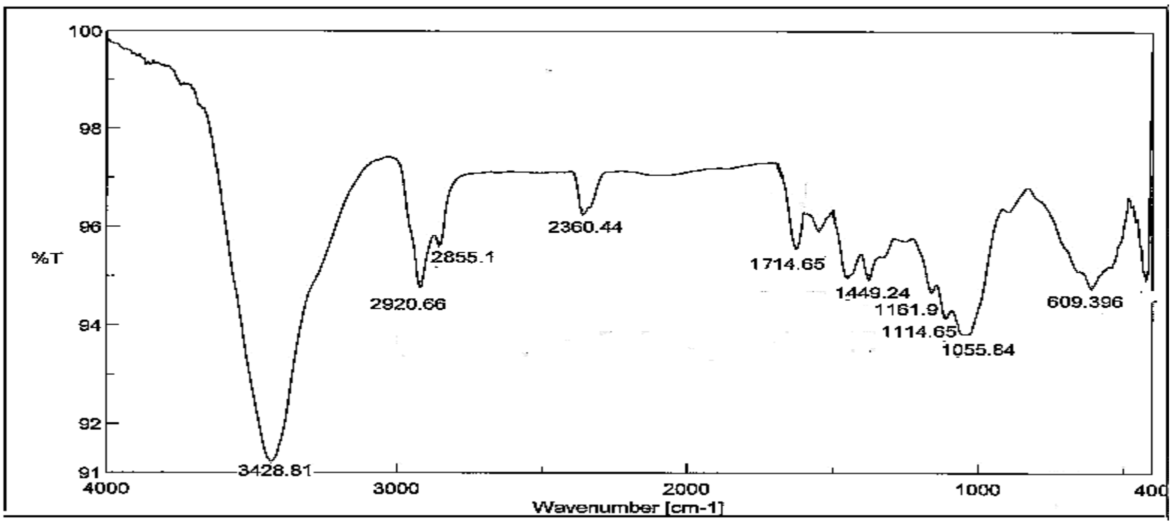


Fig. 26. FT-IR of Bit. / AO_1 (0.5%) / SBS blend after TFOT.

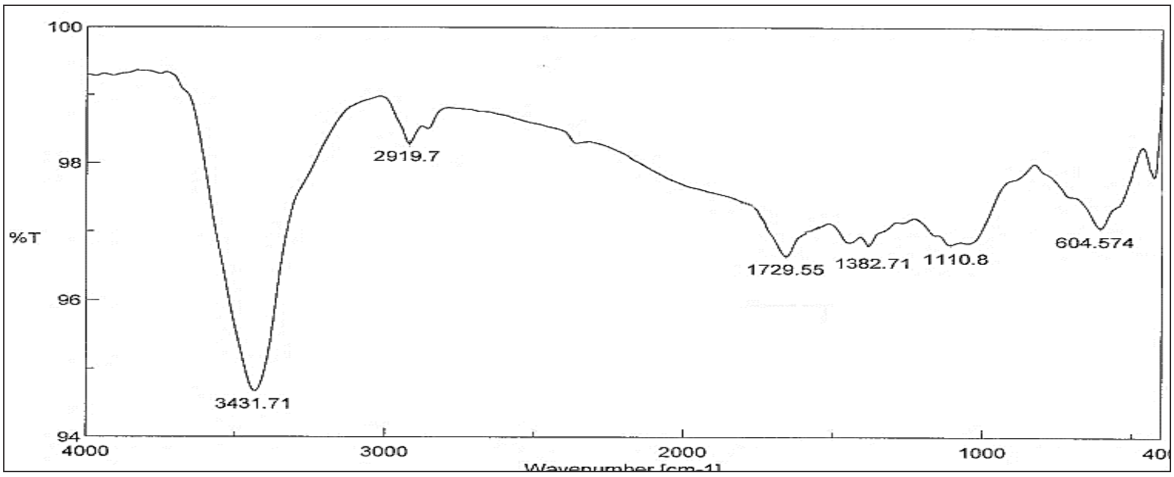


Fig. 27. FT-IR of Bit. / AO_1 (1%) / SBS blend after TFOT.

T.A.N. analysis of the prepared blends

T.A.N. increase with increasing the oxidation due to the formation of carboxylic acids results from formation of C=O group. From data in table (8), we could find that the total acid number of the base bitumen is 0.831 while it became 2.235 after aging via TFOT. When the antioxidants added separately with the different concentration ratios to bitumen and then aged via TFOT, the acidity decreases at all concentrations of all antioxidants.

The highest value of acidity was 2.049 at concentration ratio 1% of AO_2 antioxidant while the lowest value in acidity was 0.84 at concentration ratio 0.5% of AO_1 antioxidant, which near to the acidity value of the base bitumen.

When bitumen was blended with 3%SBS polymer before aging via TFOT, the acidity decreased comparing to that of the base bitumen due to the absorption of the light fraction that can easily oxidized and hence decreasing the C=O group formed and acidity decreased to be 0.616.

When SBS modified bitumen aged via TFOT, SBS degraded and the light fractions oxidized leading to formation of C=O groups which led to increasing the acidity comparing to SBSMB before TFOT to be 1.961.

The most promising antioxidant AO_1 when mixed with SBSMB then aged via TFOT, they led to decreasing the acidity of blends achieving the lowest value of acidity 1.0629 at concentration ratio 1% AO_1 antioxidant.

TABLE 8. T.A.N. of the prepared blends.

Sample	T.A.N. mg KOH/gm
Base Bitumen (B.B.)	0.831
B.B. After TF	2.325
Bit. / AO_1 (0.25%)	0.897
Bit. / AO_1 (0.5%)	0.84
Bit. / AO_1 (1%)	1.154
Bit. / AO_2 (0.25%)	1.744
Bit. / AO_2 (0.5%)	1.524
Bit. / AO_2 (1%)	2.049
Bit. /SBS before TFOT	0.616
Bit. / SBS after TFOT	1.961
Bit. / AO_1 (0.5%) /SBS	1.341
Bit. / AO_1 (1%) /SBS	1.0629

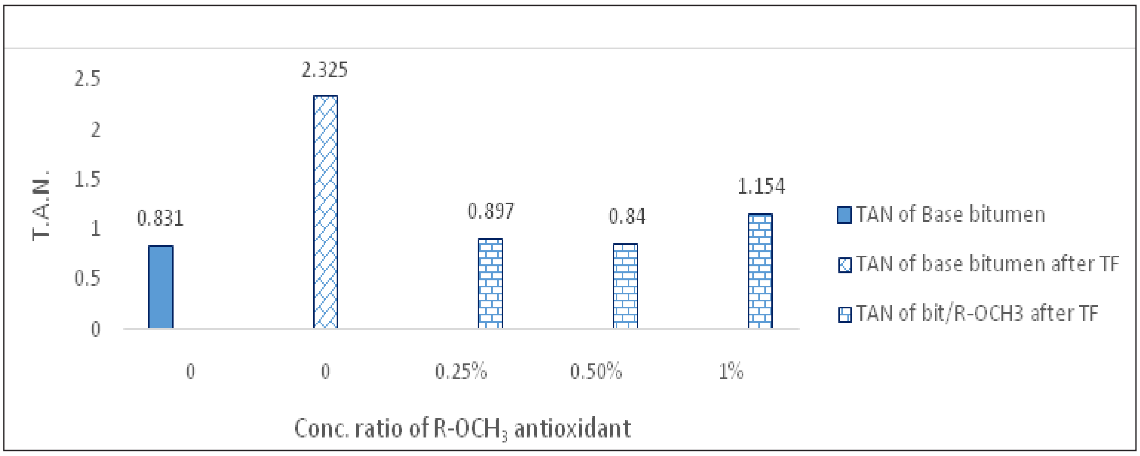


Fig. 28. T.A.N. of Bit. /AO_2 blends at different concentration ratios of AO_2 .

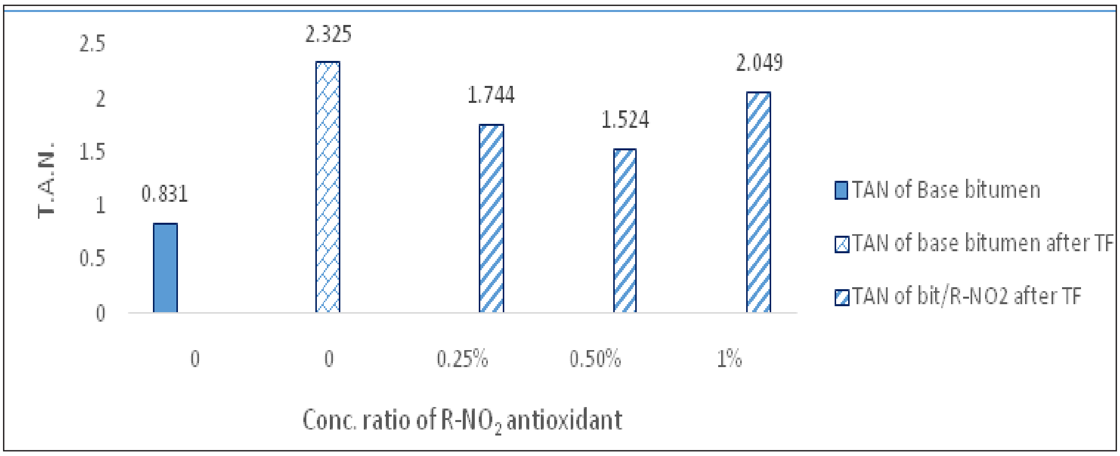


Fig. 29. T.A.N. of Bit. /AO_2 blends at different concentration ratios of AO_2.

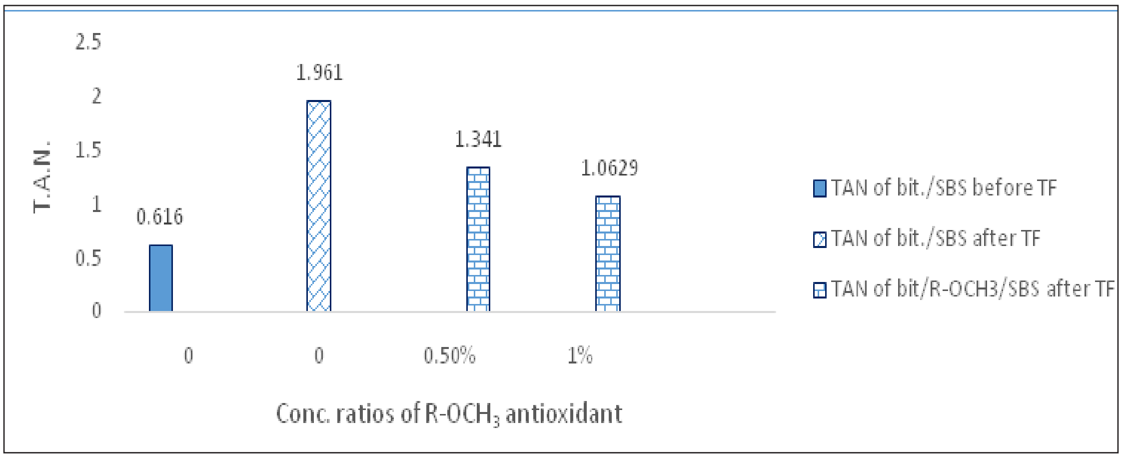


Fig. 30. T.A.N. of Bit. /AO_1/SBS blends at different concentration ratios of AO_1.

Conclusion

- The structure of the prepared antioxidants proved by the FTIR, ^{1}H-NMR and Mass spectroscopy.
- Viscosity at 135°C ST and softening point of the base bitumen after TFOT increased while penetration is decreased indicating the hardening of bitumen.
- From physical properties results, the antioxidants AO_2 when added to the base bitumen, the viscosity and softening point increased and penetration decreased comparing to the base bitumen after TFOT indicating that these antioxidants made double function as antioxidants and the remain portions act as fillers . The antioxidantAO_1 considered the best antioxidants as IT gave results nearly to that of the base bitumen.
- From T.A.N. results, all examined bitumen blends modified with antioxidants improve the oxidative aging resistance of bitumen after TFOT and the best results obtained with AO_1antioxidant at concentration ratio 0.5%.
- Viscosity and softening point increased sharply while penetration and ductility are decreased when 3% SBS was introduced to the base bitumen. But when aged via TFOT , viscosity and softening decreased while penetration and ductility comparing to those of SBS modified bitumen before TFOT. This indicate to the occurrence of the thermal oxidation that led to the degradation of the SBS polymer chain and decreasing the aging resistance of SBS modified bitumen.
- When the most promising antioxidant added separately with concentration ratios (0.5&1%) to the SBS modified bitumen then aged via

TFOT , the viscosity and softening point increased while penetration and ductility decreased comparing to those of SBS modified bitumen after TFOT indicating to that the antioxidants retard the thermal oxidation and hence improve the aging resistance of SBS modified bitumen.

- The best modification of bitumen with 3% SBS was obtained by the addition of 1% concentration ratio of $AO_1$and this not only proven by the physical properties but also by the T.A.N. and FTIR results.

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تحسين تأثير التقادم على البتيومين والبتيومين المحسن بالإستارين بيوتادين إستايرين بوليمر وذلك باستخدام مضادات اكسده محضره حديثا

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التقادم الناتج عن الأكسدة الحرارية للبتيومين له تأثير سيء على متانه غلاف البتيومين لذا فأننا في هذا البحث نهدف الى تقليل هذا التقادم من خلال تحضير مركبين هما ($R-OCH_3=AO_1$ & $R-NO_2=AO_2$) واختبار هذه المركبات كمضادات اكسده. تم فحص هذه المركبات عن طريق الأدوات الطيفية التقليدية للتحليل مثل الاشعة تحت الحمراء والرنين المغناطيسي النووي البروتوني. تم خلط هذين المركبين كلا على حده مع البتيومين ذو درجة (٧٠/٦٠) عند نسب تركيزات مختلفة (٠,٢٥ و٠,٥ و ١٪) ثم عمل تقادم للخلطات من خلال اختبار الطبقة الرقيقة عند درجة حرارة ١٧٠ د س لمدة ٥ ساعات. تم تقييم تأثير هذه المركبات من خلال التغير في نواتج الاشعة تحت الحمراء والعدد الكلى للأحماض والخواص الفيزيائية للبتيومين قبل وبعد الاكسدة الحرارية. أوضحت النتائج ان نسبة ٠,٥ و ١٪ أعطت أحسن النتائج في تحسين البتيومين. بعد ان يتم تعديل البتيومين بهاتين النسبتين تم إضافة ٣٪ ستايرين بيوتادين ستايرين بوليمر ثم عمل تقادم للخلطات من خلال اختبار الطبقة الرقيقة عند ١٧٠ د س لمده خمس ساعات. تم تقييم تأثير مضاد الأكسدة هذه في تقليل التقادم للبتيومين المعدل بالبوليمر وذلك من خلال التغير في نتائج الأشعة تحت الحمرا والعدد الكلى للأحماض والخواص الفيزيائية للبتيومين قبل وبعد الأكسدة الحرارية. أوضحت النتائج ان افضل تحسين للبتيومين المعدل بالبوليمر كان عند تركيز ١٪ من مضاد الأكسدة AO_1.