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Flow Ability Enhancement of Waxy Crude Oil Using New Spirocompound Based on Aromatic Amine System

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THIS work was focused on an investigating of flow ability of waxy crude oil by nontraditional polymer compound. For this propose, a spirocompound consisted of benzaldehyede and triethanolamine 6,6'-(((phenylmethylene) bis (oxy)) bis (ethane-2,1-diyl)) bis (2-phenyl-1,3,6-dioxazocane) [SB1] was synthesized using zeolite as a catalyst. The chemical structure of the [SB1] was investigated by FT-IR, TGA,GPC, H1NMR and Mass spectroscopy. The rheological behavior and pour point depression of waxy crude oil were also studied different dosages and temperatures. The results showed a significant reduction in the viscosity at different temperatures and dosages. Moreover, it was noticed a decrease in the apparent viscosity and the Bingham yield value for [SB1] 437.7, 367.1, and 307.1 cp and 0.48, 0.39 and 0.31 Pa at 15 ºC, 20 ºC and 30 ºC and concentration 1000 ppm respectively. While the blank experiment displayed 743.1, 694.2 and 607.2 cp and 0.74, 0.69 and 0.60 Pa at the same temperatures. This study included blends between [SB1] and the acrylate based polymers abbreviated as (B1, B2, B3 and B4). Furthermore, the rheological behavior and the pour point for these blends exhibited that the blend [B4] shew more reduction in the apparent viscosity than [SB1] being alone. The apparent viscosity and yield value for [B4] were; 267.8, 249.2 and 212.7 cp and 0.22, 0.11 and 0.09 Pa at 15ºC, 20ºC and 30ºC and concentration 1000 ppm respectively. The pour point depression (Δpp) of [SB1] was 9ºC while the blank pour point was 27 ° C and the B4 was achieved the maximum depression in the pour point (Δpp= 18 ° C) at a concentration of 1000 ppm. This result means that the addition of [SB1] to [B4] showed the most positive synergistic effect.

Keywords: Spiro compound, Wax Crude Oil, Pour Point, Rheology, Physical Blends.

Introduction

Crude oil transportation is considered as a difficult and extremely technical operation. More efficient and commercial methods are required to deal with the high viscosity which represents the main difficulties in the pipeline transportation **[1-9].** Its well-known that, wax crude oils carries a high viscosity and a high pour point make the production, transportation and refining operations more difficult, especially at a low temperature. The wax crystals are generated at a definite temperature that is below the solubility boundary temperature of the oil solution, causing a negative impact on the crude oil properties. Furthermore, cooling process causes formation of the crystal networks that dispersion of wax crystal with higher saturated crude oil. Indeed, the heavy fraction likes wax, asphaltenes, and resin associated with formation the solid phase. These wax crystals grow in size until the whole inner wall of the pipeline is covered with wax layers, causing reduction of flow and extra burden on the pumping system. Therefore, in order to reduce the heavy crude viscosity in the pipeline transportation process several methods could be used such as chemical additives, heating and dilution with alcohols or lighter crudes **[10]**. The

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typically chemical additives are polymers, having a wax-like paraffinic part and charged component, such as polyalkyl acrylates and methacrylate's, ethylene vinyl acetate copolymers, copolymers and homo of alpha olefins, alkyl fumarate-vinyl acetate copolymers and alkyl esters of styrene-maleic anhydride copolymers **[11-15]**.

Shijun Chen et al., **[16]** stated that, the process of oil refinement contains negative factors that represented by large molecular weight, long molecular chain, and high thermo stability of these polymers. In this context, the small molecular additives of crude oil are necessary to act as a viscosity reducer. Recently, the structural properties of gelled waxy crude oils are carefully investigated to restart the pipeline transportation of oils **[17, 18]**. The yielding process of statically cooled waxy crude oils was investigated by Chang et al., **[19]** who developed a model with elastic-limit, dynamic, and static yield stresses to illustrate the yielding process. The first object of this work was an application of a non-polymer compound to promote the flow ability of waxy crude oil and to decrease its pour point degree. Therefore, a spirocompound 6,6'-(((phenylmethylene) bis (oxy)) bis (ethane-2,1-diyl)) bis (2-phenyl-1,3,6-dioxazocane) was prepared. The study of rheological behavior and pour point depression of this compound with waxy crude oil was the second object. Moreover, illustrative mechanism was used to understand the effect of this spirocompound as a flow improvement of waxy crude oil.

Materials

Benzaldhyde (99.5%) and Triethanolamine (99 %), were obtained from Sigma-Aldrich. Zeolite (99 %) and Para-Toluene Sulphonic acid as a catalysts (99 %) were obtained from El-Gomhouria Company, Egypt. The solvents including Xylene (99 %), Isopropanol (99 %), Toluene (99 %), Methanol (99 %) and Ethanol (99 %) were purchased from Adwic Chemicals Company, Egypt). The waxy crude oil (NQ-4) was collected from North Qarun Petroleum Company, Egypt) without any treatment. The physicochemical properties of the NQ-4 oil were displayed **Table 1**.

Preparation and Methods

Synthesis of 6,6'-(((phenylmethylene) bis (oxy)) bis (ethane-2,1-diyl)) bis (2-phenyl-1,3,6-dioxazocane) [SB1]

A molar ratio (3:2) of Benzaldehyde [318.36 gm] and Triethanolamine [298.38gm] was prepared in a flask (250 1L) contain 100 ml Xylene as a solvent. Zeolite 5 % (wt) was added to the mixture as a catalyst **[20]**. The components were refluxed at 180 ˚C for about 8h. The pure product was obtained by filtration Zeolite and for solvent evaporation **[21]**. The final product was named 6, 6'-(((phenylmethylene) bis (oxy)) bis (ethane-2,1-diyl)) bis (2-phenyl-1,3,6-dioxazocane) [SB1]. The reaction was illustrated in **Scheme1.**

Preparation of poly octadecyl acrylate co-maleic anhydride

According to Alsabagh et al., **[21],** ODA (20 gm), MA (6 gm) and 58 ml Toluene were add on a magnetic stirrer at 70°C with benzoyl peroxide (0.27 gm) for 4 h. Thus, the polymer was physically mixing with the [SB1] to make a blend [B1].

Esterification and Amidation of (octadecyl acrylate)-co-(maleic anhydride)

As reported by Alsabagh et al., **[21],** Octadecyl alcohol and (octadecyl acrylate)-co-(maleic anhydride) esterification reaction was achieved in a round four-necks flask (150 ml) equipped with N2-line, reflux condenser, magnetic stirring and a Dean Stark apparatus. P-toluene sulphonic acid (1%) was added to 25 ml of Xylene and further heated up to 125 °C. Furthermore, a 2 mol of octadecyl alcohol and octadecyl acrylate co-maleic anhydride was supplemented. The amidation of Octadecyl alcohol and octadecyl acrylate co-maleic anhydride with 2,4,6-trinitrobenzene sulfonic acid was carried out according to the above estrification process **[21]**. The ester and the Amid polymer were mixed physically with the [SB1] to obtain the blend [B3 and B2], respectively. Moreover, the SB1 was also blended with the commercially currently used pour point dispersant from CSDC center at the Egyptian Petroleum Research Institute EPRI –J 25 **[22]** to obtain the blend [B4].

Used Techniques

Fourier Transformer Infrared (FT-IR):

The FTIR spectra were recorded using Thermo Fisher Scientific Spectrometer (Nicolet Is-10 in the range of 400- 4000 cm^{-1}).

The ^{1}H-NMR spectra: Varian VXR-300 multinuclear pulsed NMR spectrometer running at

300 MHz ^{1}H resonance frequency (recorded at 30°C) was applied.

Mass Spectrum: This method was carried out on direct controller inlet part to single quadropole mass analyzer in (Thermo Scientific GCMS) model ISQ LT using thermo-x-calibur software.

Gel Permeation Chromatography (GPC): Model waters 515/2410Gel Permeation Chromatograph (GPC, Waters, America) was used.

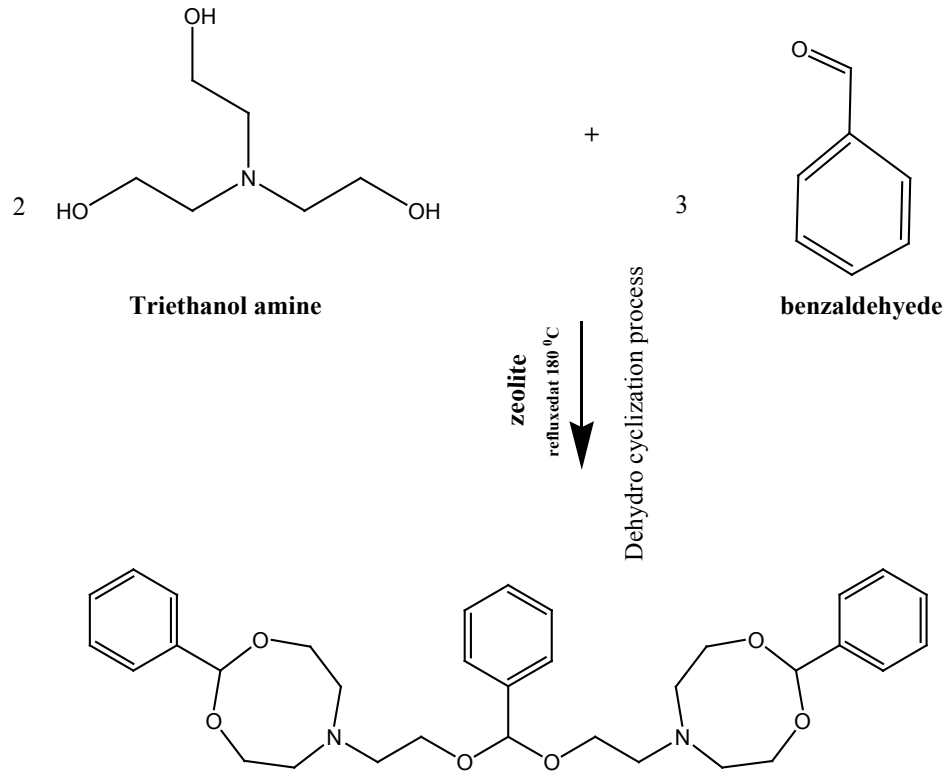
The thermal Gravimetric analysis (TGA) This technique was undertaken by simultaneous thermal analyzer, TA SDT Q600 V20.5 Build 15. About 6-8 mg were placed in aluminum pan.

Rheological Measurements:

PVS Rheometer ″Brookfield″ was utilized to study the rheological behavior for the treated and the untreated crude oil with ″SB1″ and their blends at different concentrations from 500 to 2000 ppm (10% active material) and at different temperatures 15, 20 to 30◦c.The geometry of B5 for use with PVS Rheometer (sec-1 / RPM=0.85) Annulus (inches/cm) =0.095(0.241) with sample volume 25 ml. The flow curve was analyzed using the Herschel-Bulkley equation: where Ꚍ is the sheer stress Ꚍ$_b$ is Bingham yield value ؛ K is the consistency index؛ m is the shear thinning index and D is the shear rate: Ꚍ=ꚌB + K D^m **[23]**. **Pour Point Measurement:** This instrument was used to determine the pour point were standard pour point test apparatus thermometer, test tubes and water bath (ASTM D97-93) **[24]**.

Results and Discussion

Structure confirmation of (SB1): **Figure 1** showed the **FT-IR spectra** of the (SB1), by inspection of the spectrum it was found that, the absorption bands at 2920 and 2852 cm^{-1}, refer to (CH_3) and (CH_2) of the alkyl groups. The beak at 1600 and 1500 cm^{-1} (C=C stretching of



6,6'-(((phenylmethylene)bis(oxy))bis(ethane-2,1-diyl))bis(2-phenyl-1,3,6-dioxazocane)

Scheme1.Preparation of Spirocompound [SB1] based on Benzaldehyde and Triethanolamine.

TABLE 1. Physicochemical Properties of The NQ4 Crude Oil

Test	Method	Result
API gravity at 60 °F	ASTMD-1298	34.3
Specific gravity at 60/60F	ASTMD-1298	0.8534
Wax content (wt%)	UOP46/64	3.2
Paraffin content	UOP46/85	7.4
Asphaltene content (wt%)	IP143/84	1.847
Kinematic viscosity, (cSt)at 40	ASTM D-445	6.336
Pour point,°C	ASTM D-97	27

TABLE 2. Yield Point and Apparent Viscosity of the SB1 and its Blends At Different Temperature and Concentration 1000 ppm

Sample name	Tmp. °C	Yield Point (Pa)	Apparent Viscosity
[Blank]	15	0.74	743.1
	20	0.69	694.2
	30	0.60	607.2
[SB1]	15	0.48	437.7
	20	0.39	367.1
	30	0.31	307.1
J 25	15	0.63	530.3
	20	0.60	500.8
	30	0.56	484.6
PODA	15	0.65	554.9
	20	0.62	539.1
	30	0.56	510.2
PODA-NH2	15	0.68	570.7
	20	0.64	561.3
	30	0.57	547.8
PODA-OH	15	0.61	493.8
	20	0.56	403.2
	30	0.50	391.7
[B1]	15	0.39	440.4
	20	0.30	398.5
	30	0.26	308.4
[B2]	15	0.29	386.5
	20	0.23	349.7
	30	0.22	258.6
[B3]	15	0.24	249.3
	20	0.19	223.5
	30	0.12	189.2
[B4]	15	0.22	267.8
	20	0.11	249.2
	30	0.09	212.7

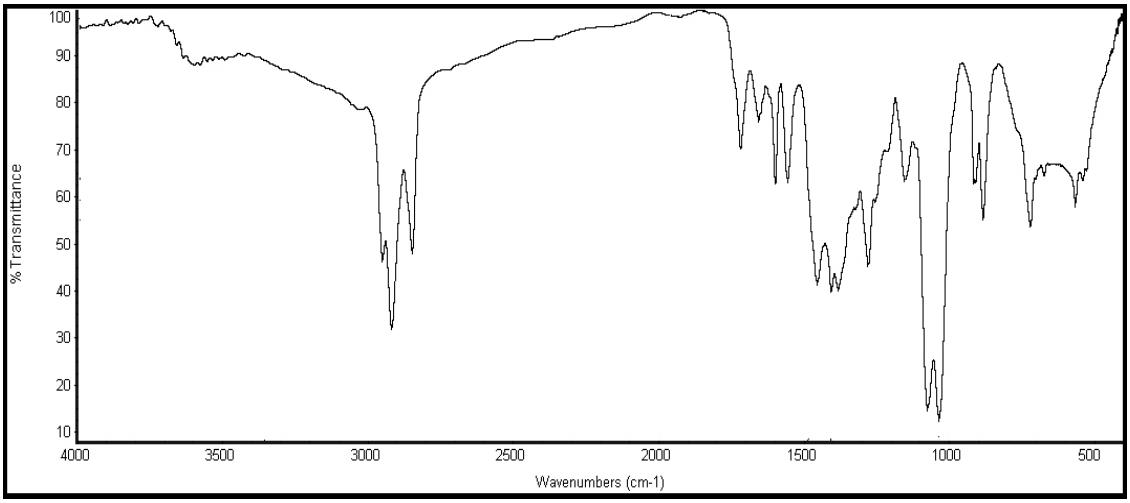


Fig. 1. FT-IR Spectra of 6,6'-(((phenylmethylene)bis(oxy))bis(ethan-2,1-diyl))bis(2-phenyl-1,3,6-dioxazocane) (SB1)

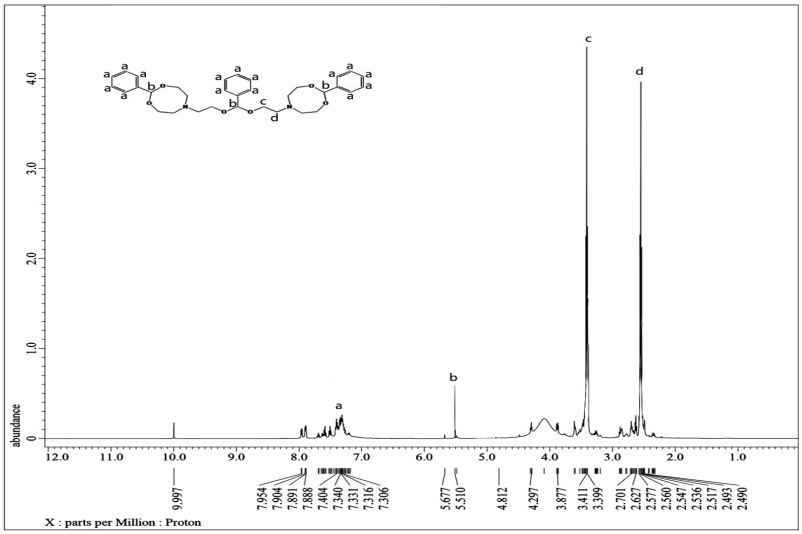


Fig. 2. H[1]NMR Spectra of 6,6'-(((phenylmethylene)bis(oxy))bis(ethan-2,1-diyl))bis(2-phenyl-1,3,6-dioxazocane) (SB1)

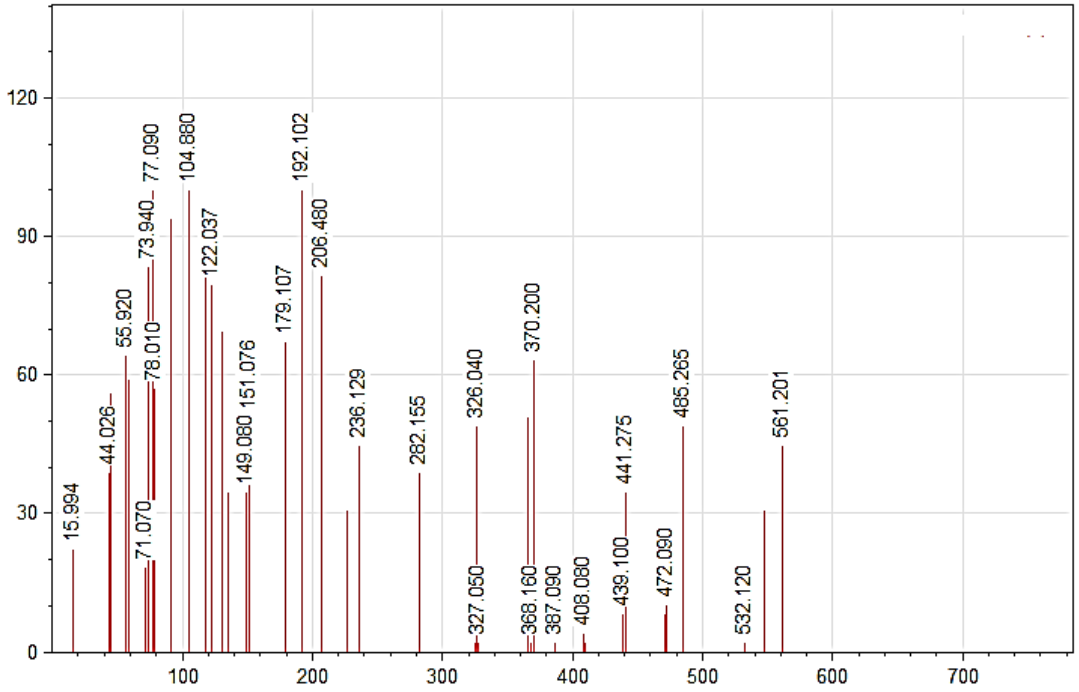


Fig. 3. Mass Spectra of 6,6'-(((phenylmethylene)bis(oxy))bis(ethan-2,1-diyl))bis(2-phenyl-1,3,6-dioxazocane) (SB1)

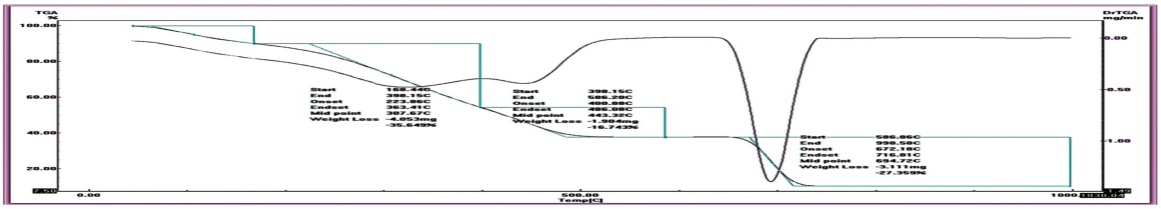


Fig. 4. TGA of 6,6'-(((phenylmethylene)bis(oxy))bis(ethan-2,1-diyl))bis(2-phenyl-1,3,6-dioxazocane) (SB1)

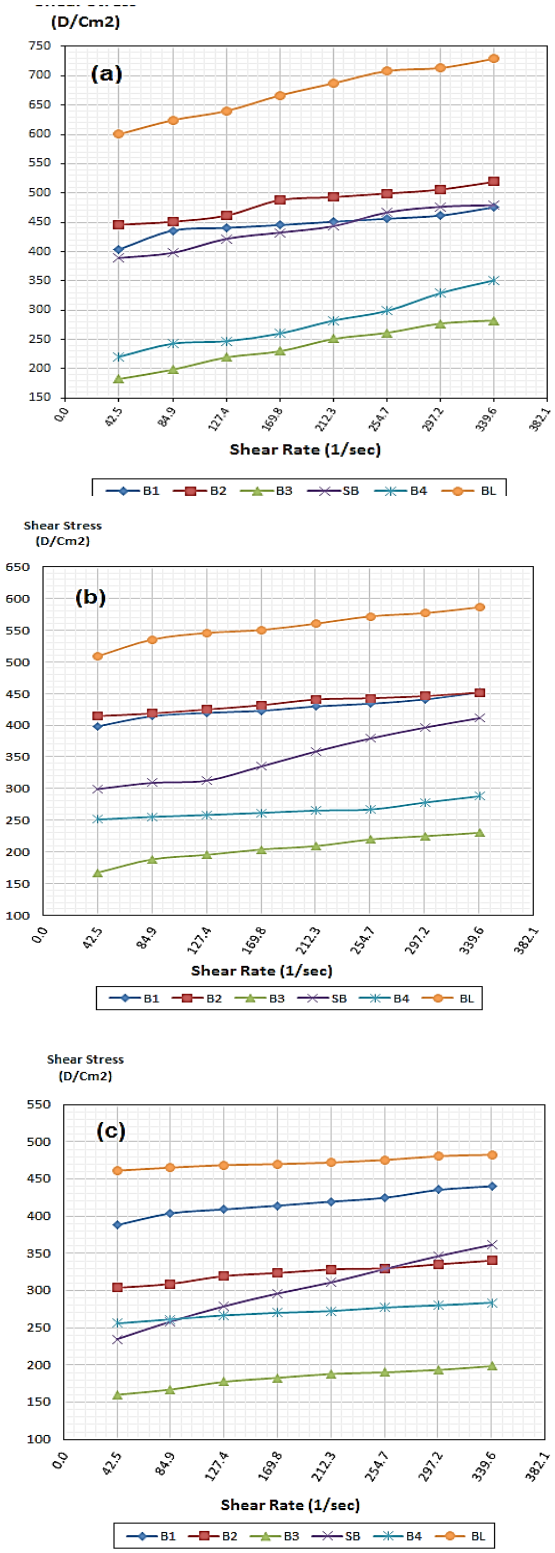


Fig. 5. Relation Between Shear Rate (1/sec) and Shear Stress (D/ Cm2) for Treated and Untreated Crude Oil at Concentration 1000 ppm at Temperature a) 15°C, b) 20°C, c) 30°C

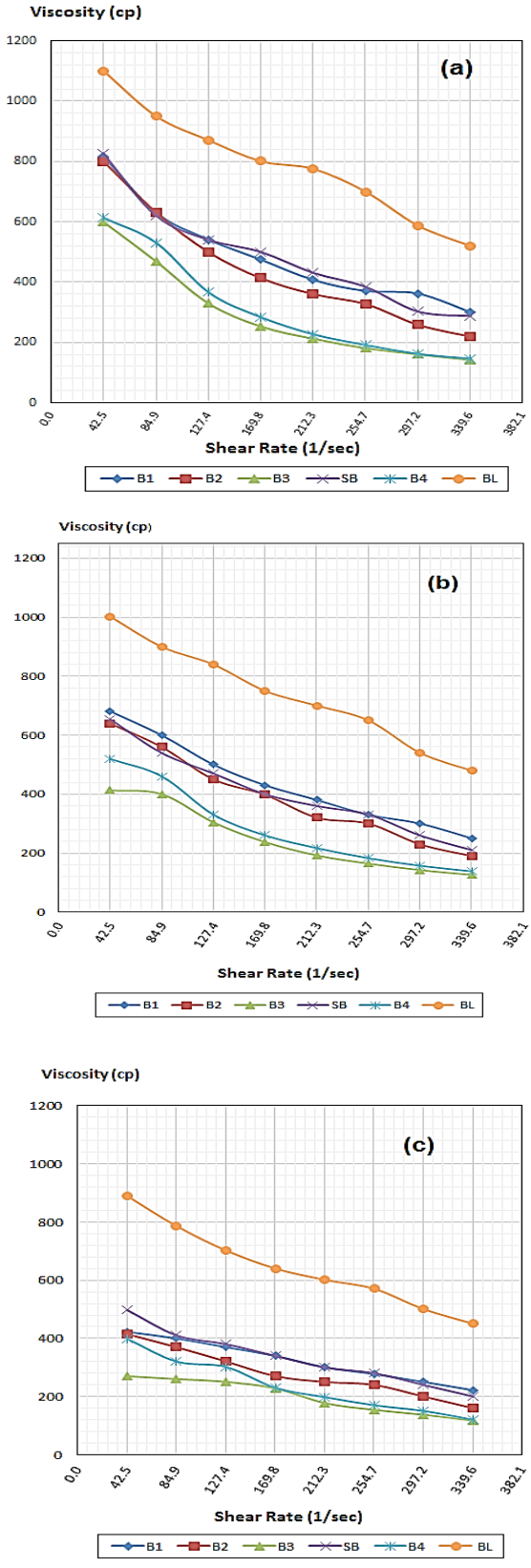


Fig. 6. Relation Between Shear Rate (1/sec) and Viscosity (Cp) for Treated and Untreated Crude Oil at Concentration 1000 ppm at Temperature a) 15 °C, b) 20°C, c) 30°C

aromatic). Also the beaks at 1000 and 1175 cm^{-1} were referred to the ethereal groups (C−O−C stretching). While the spectrum at 1300 cm^{-1} was referred to (C−N−C stretching).

The **NMR spectrum** as illustrated in **Fig. 2,** the SB1 demonstrated multiple peaks at chemical shift δ 7.22 to 7.52 protons a (m, 10H) indicated to the aromatic H^1 of phenyl groups. The chemical shift δ 5.48 (d,1H) donated methane group between two oxygen atoms (O−$\underline{CH_2}$−O), 3.47(t, 2H) for methylene group (O−$\underline{CH_2}$−CH_2), and the chemical shift δ 2.53(t, 2H) for methylene (N−$\underline{CH_2}$−CH_2). The single peak at 5.48 (d, 1H) was due to the α-H of the ($\underline{CH_2}$−O−$\underline{CH_2}$−O), which was inducted by two oxygen atoms resulting in the relatively high chemical shift. The four [CH_2] groups appeared at different chemical shifts were resulted from the change of the chemical structure environments which make different shift of the hydrogen protons.

Figure 3 described the Mass spectra Fragmentation of Compounds (SB1). Mass Spectra Fragmentation of (SB1) $C_{33}H_{42}N_2O_6$ M.wt 562 showed a base peak at molecular weight 561 MS: m/z = ($C_{33}H_{42}N_2O_6$-561) ($C_{27}H_{37}N_2O_6$ - 485.265) (C_6H_5 -77.0391) ($C_{21}H_{33}N_2O_6$ - 409.234) ($C_{13}H_{18}NO_3$ - 236.129) ($C_9H_{11}O_2$- 151.076) ($C_{21}H_{14}NO$- 448.265) ($C_{26}H_{36}N_2O_6$- 472.257) ($C_{12}H_{16}NO_2$ -206.48) ($C_8H_{16}NO_3$- 174.113) ($C_{21}H_{26}NO_4$ - 356.186) ($C_6H_{14}NO_2$- 132.102) ($C_{11}H_{14}NO_2$ -192.102) ($C_6H_{14}NO$ -116.108) ($C_{12}H_{16}NO_4$ - 206.118) (C_7H_7 - 91.0548) (C_6H_6. - 78.047) (C_3H_6NO. - 72.044) ($C_6H_{14}NO_2$ - 132.102) ($C_4H_9O_2$ - 89.06) (C_3H_8 N. - 58.067) (.CH_3 - 15.02) (C_7H_7 – 91.0548). It is also clear that, the intensity fragment proved the (SB1) synthesis.

Figure 4 reveled the **Thermal Gravimetric Analysis TGA** of the (SB1). This result showed that, the (SB1) was a stable compound below 168 °C, but as the temperature increase above 205 °C, the crystal started to lose its weight sharply on the three different stages. The stage one from 200 to 400°C the (SB1) loosed 35.6 % of weight but in the stage two, from 400 to 700 °C the (SB1) loosed 16.6 % from their weight and in the stage three above 700 °C the (SB1) loosed 27.3%.This mean that the (SB1) compound was thermally stable product and very stable during the application process in the petroleum industry.

Rheological Properties

The rheological behavior of NQ4 crude oil, at the temperature below and above the pour point (15, 20 and 30°C), was listed in **Table 2.** The data revealed that, the crude oil without additives followed the non-Newtonian behavior as shown in **Fig. 5&6**. By inspecting the data in **Table 3**, it appeared that the values of the apparent viscosity (η_{app}) of the blank NQ4 crude oil were of 743.1, 694.2 and 607.2 **(cp)** and the yield stress (τ_B) values were of 0.74, 0.69 and 0.60 Pa at temperatures of 15, 20 and 30 °C, respectively at a concentration of 1000 ppm. A decrease in the η_{app} was obtained by adding the [SB1] where η_{app}values were of 437.7, 367.1 and 307.1**(cp)** accompanied with Bingham yield stress (τ_B) values were of 0.48, 0.39 and 0.31 Pa at the same temperatures 15°C, 20°C and 30°C, respectively at a concentration of 1000 ppm. Mean while the depression was 17.9%. **Table 2** demonstrated**,** the best yield value (τ_B), that was also exhibited with the bland B4 with increasing temperature, it was; 0.22, 0.11 and 0.09 against 15°C, 20°C and 30°C. The improved of rheological properties by the [SB1] was recorded in the petroleum application and the suggested mechanism is shown in **Fig. 7.** The mechanism based on Van der Waals Forces attraction and repulsion the polarity of benzene rings (3 rings) and the presence of high polarity of oxygen and nitrogen in the same molecular represented an important role in the activity of the compound. The multiphenyl groups can interact with asphaltene by π-π stacking, and the Spiro structure can fix the stacking in different direction, which can prevent the agglomeration of wax crystals in crude oil. The high flow ability and solubility of the waxy crude oil are achieved by the (SB1) due to the presence of benzene rings which effectively reduce the wax network formation. Thus the solubility of waxy crude oil was enhanced in its low chain paraffin's. The yield values of J25, PODA, PODA-NH_2 and PODA-OH in **Table 2** were 0.63, 0.65, 0.68 and 0.91 pa at15°C, 20°C and 30°C compared with the [SB1] at the same temperature (0.48) pa. The blinds; B1, B2, B3 and B4 displayed the yield values at 15°C; 0.39, 0.29, 0.24 and 0.22 pa. This result; means that positive synergism was obtained between these mixtures to improve the flow properties, and pour point.

The highest efficiency was accomplished by the [B4] and the[B3] where apparent viscosity and the yield value displayed more reduction in comparison to the [SB1] alone. The data for the [B4] was (η_{app}) 267.8, 249.2 and 212.7 **(cp),** (τ) 0.22, 0.11 and 0.09 at a temperatures of 15°C,

TABLE 3. Dynamic viscosity of the SB1 and its Blends at different concentrations 500,1000,2000 ppm and different temperatures (15°C,20°C,30°C)

Sample name	Tmp.°C	Viscosity at different concentrations ppm			Blank [BL]
		500	1000	2000	
	15	900.60	824.64	796.60	1345.5
[SB1]	20	736.45	654.80	632.50	1197.4
	30	599.1	497.70	390.10	890.3
	15	877.65	815.30	750.50	1345.5
[B1]	20	716.94	681.55	610.20	1197.4
	30	512.52	422.36	345.5	890.3
	15	815.65	800.16	726.20	1345.5
[B2]	20	698.11	640.13	601.33	1197.4
	30	498.50	414.90	302.30	890.3
	15	660.30	599.20	501.10	1345.5
[B3]	20	508.30	413.60	399.30	1197.4
	30	398.40	270.10	196.10	890.3
	15	786.30	613.50	531.60	1345.5
[B4]	20	601.00	519.90	450.30	1197.4
	30	418.36	398.70	320.30	890.3

TABLE 4. Pour point of the SB1 and its Blends at different concentrations ppm

Sample name	PPT different concentrations ppm						Blank[BL]
	500	Δpp	1000	Δpp	2000	Δpp	
[SB1]	21°C	-6°C	18°C	-9°C	15°C	-12	27°C
PODA	24	-3°C	21	-6°C	21	-6°C	
PODA-NH2	24	-3°C	24	-3°C	21	-6°C	
PODA-OH	21	-6°C	18	-9°C	18	-9°C	
J25	18	-9°C	15	-12°C	15	-12°C	
[B1]	18°C	-9°C	15°C	-12°C	12°C	-15	
[B2]	21°C	-6°C	18°C	-9°C	15°C	-12	
[B3]	15°C	-12°C	12°C	-15°C	9°C	-18	
[B4]	12°C	-15°C	9°C	-18°C	6°C	-21	

Δpp Pour point depression, °C remain sign decreasing value of pour point from blank 27°C

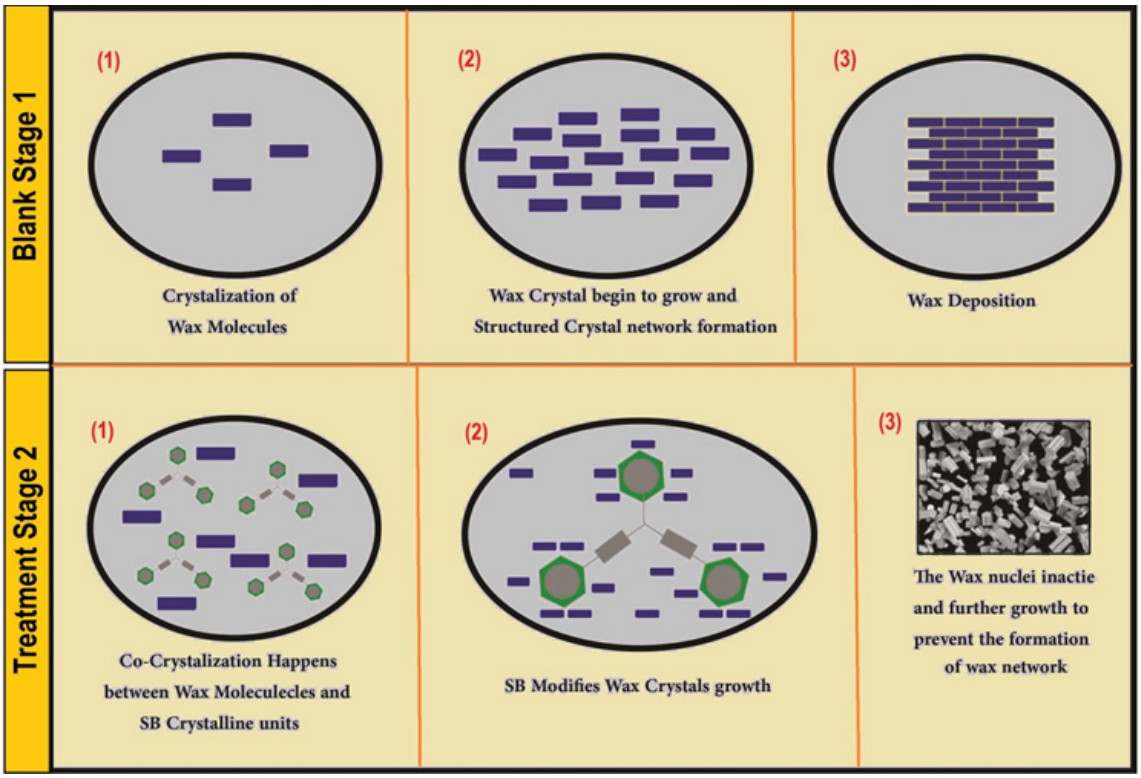


Fig. 7. Mechanism of Disperssion of Paraffin Wax Crude Oil by [SB1]

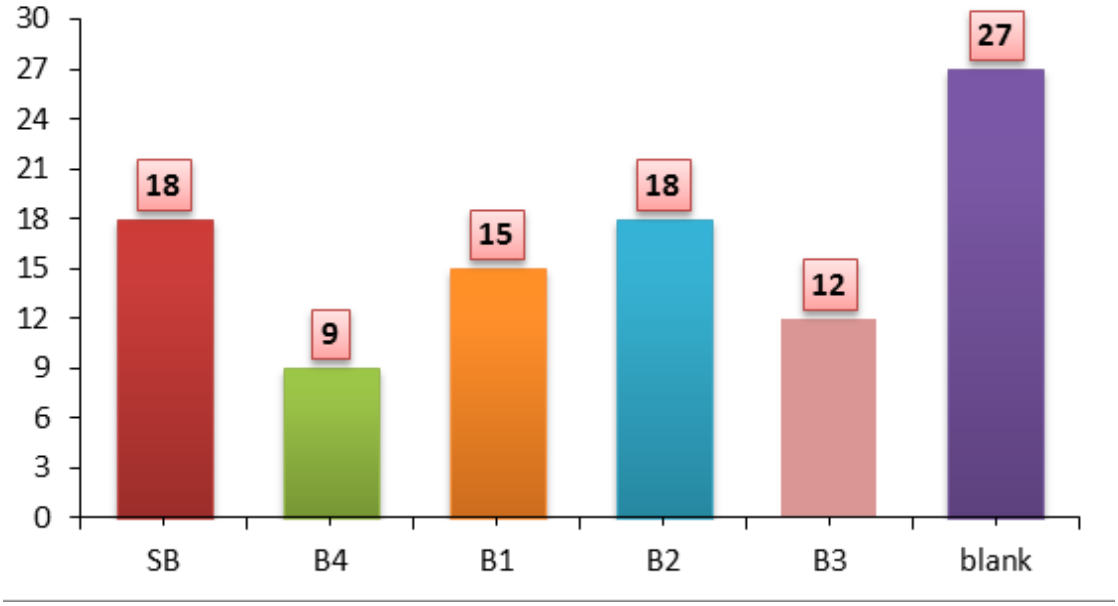


Fig. 8. Pour point degree of [SB1] and its blends at concentration 1000pp

20°C and 30°C, respectively and at a concentration of 1000 ppm. Furthermore, the data for the [B3] was (η_{app}) 249.5, 223.5 and 189.2**(cp),** (τ) 0.24, 0.19 and 0.12 at temperatures of 15°C, 20°C and 30°C, respectively. **Table 3** exhibited the dynamic viscosities of the untreated and the treated crude oil at different concentrations. Moreover, by analyzing th**e** presented results (see **Table 2)**, it was found that, generally by the increasing in the temperature the apparent viscosity was decreased. At the same time the increases of additive dosage decreased the apparent viscosity.

Effect of spirocmpound on pour point of waxy crude oil:

Depression in the pour point is generally attributed to the modification of wax crystal. The (SB1) induced a spectacular reduction in the pour point of the crude oil by preventing wax deposition. **Fig. 8** and **Table 4** cleared that the pour point of crude oil was decreased by the (SB1) from 27 °C to 18°C. The benzene rings played an important role in the inhibition of the wax crystals growthing in the structure. The wax crystal can adsorb on the different direction of the (SB1) molecule. The adsorption wax molecule derived the wax nuclei inert and further growth to prevent the formation of wax network. Hence, the wax crystal molecules were existed in a fine small size or at a high dispersion in the crude oil, therefore the net like structure, which is necessary for solidification, was inhibited **[23]**.

As the result of the flow of crude oil enhanced consequently the pour point was depressed. This mechanism nearly described our obtained data as mentioned before in **Table 4.** In **Table 4,** the (SB1) increased the pour point depressant (Δ PP= 9°C). Otherwise the (SB1) blend the (B4) achieved the pour point depressant of, (Δ PP= 18°C) which exhibited the pour point 12°C, 9°C and 6°C at the concentrations of 500, 1000 and 2000 ppm respectively.

Conclusion

- Aspirocompound 6,6'-(((phenylmethylene) bis (oxy)) bis (ethane-2,1-diyl)) bis (2-phenyl-1,3,6-dioxazocane) (SB1) was prepared to enhance the flow ability of waxy crude oil and decrease its pour point.
- The chemical structure of the [SB1] was investigated by FT-IR, TGA,GPC, H^1NMR and Mass spectroscopy.
- The [SB1] displayed η_{app}values 437.7, 367.1 and 307.1**(**m.pa) accompanied with Bingham yield value (τ_B) values 0.48, 0.39 and 0.31 Pa at temperatures 15°C, 20°C and 30°C, respectively and at a concentration of 1000 ppm.
- The [B4] exhibited more reduction than the [SB1] alone, where the apparent viscosity and the yield value for the [B4] were (η_{app}) 267.8, 249.2 and 212.7 (m.pa**),** (τ) 0.22, 0.11 and 0.09 at temperatures of 15°C, 20°C and 30°C, respectively and at a concentration of 1000 ppm.

References

1. Newberry, E. M., Chemical effects on crude oil pipeline pressure problems. *Journal of Petroleum Science & Technology*. **36,** 779–786 (1984).

2. Emad, A., Soliman, E.A., Elkatory, M. R., Hashem, A.I., Ibrahim, H.S., Synthesis and performance of maleic anhydride copolymers with alkyl linoleate or tetra-esters as pour point depressants for waxy crude oil. *Fuel*. **211,** 535–547 (2018).

3. Huang, H., Wang, W., Peng, Z., Li, K., Gan, D., Zhang, S., Ding,Y., Wu, H., Gong, J., The effect of cooling processes on the yield stress of waxy model oil with nanocomposite pour point depressant**.** *Journal of Petroleum Science and Engineering.* **175,** 828–837 (2019).

4. Lia, N., Maoa. G., Wua,W., Liub, Y., Effect evaluation of ethylene vinyl acetate/nano-montmorillonite pour-point depressant on improving the flow properties of model oil**.** *Colloids and Surfaces.* **555**, 296–303 (2018).

5. Sivakumar, P., Sircar, A., Deka, B., Silviya Anumegalai, A., Suresh Moorthi, P., Yasvanthrajan, N., Flow improvers for assured flow of crude oil in midstream pipeline a review. *Journal of Petroleum Science and Engineering*. **164,** 24-30 (2018).

6. El-Nagar, R.A., Attia, S.K., Rizk, S.A., Osman, D.I., Abdallah.,R.I., Rheological and Physical Properties of Ionic Liquids with Ammonium Cations as Synthetic Lubricants*. Egypt. J. Chem.* 2**(61),** 349 – 360 (2018).

7. Al-Sabagh, A. M., Nasser, N. M., Mahmoud, T., Investigation of Kinetic and Rheological properties for the demulsification process. *Egyptian Journal of Petroleum.* **22(1),** 117–127 (2013).

8. Allen, T.O., Roberts, A.P., Production Operations. *Tulsa, Oklahoma: Oil and Gas Consultants International,* second edition. **2, (**1982).

9. Deka, B., Sharma, R., Mandal, A., Mahto, V., Synthesis and evaluation of oleic acid based polymeric additive as pour point depressants. *Journal of Petroleum Science and Engineering.* **170,** 105-111 (2018).

10. Hasan S. W., Ghannam, M.T., Esmail, N., Heavy crude oil viscosity reduction and rheology for pipeline transportation. *Fuel.* **89**(5), 1095-1100 (2010).

11. Gu, X., Zhang, F., Li, Y., Zhang, J., Chen, S., Qu, C., Chen,G. Investigation of cationic surfactants as clean flow improvers for crude oil and a mechanism study. *Journal of Petroleum Science and Engineering*. **164**, 87-90 (2018).

12. Ahmed, A.S., Nassar, A. M., Nassar, R. M., Khattab, A. F., Abdel-Azim, A.-A. A., Synthesis and Evaluation of Some Polymeric Compounds as Pour Point Depressants and Viscosity Index Improvers for Lube Oil. *Journal Petroleum Science and Technology.* **26**(12), (2008).

13. Al-Sabagh, A. M., El-Hamouly, S.H., Khidr, T.T., Khidr, T.T., El-Ghazawy, R.A., Higazy, Sh.A., Synthesis of phthalimide and succinimide copolymers and their evaluation as flow improvers for an Egyptian waxy crude oil. *Egyptian Journal of Petroleum*. **22,** 381–393 (2013).

14. Popoola, C. A., Ayo, J.A., Adedeji, O. E., Akinleye, O., Triethanolamine (TEA) As Flow Improver For Heavy Crude Oils. *Journal of Applied Chemistry (IOSR-JAC).* **3** (8), 34-38 (2015).

15. Al-Sabagh, A. M., Khidr, T.T., Moustafa, H. M., Mishrif, M.R., Al-Damasy, M.H., Investigating the synergistic effect between oil soluble surfactants and styrene–maleicanhydride copolymers to enhance the flow properties of waxy crude oil. *Petroleum Science and Technology*. **33**, 1381-1388 (2017).

16. Chen, S., Zhao, K., Chen, G., Bai, L., Feng, L., Synthesis and Application of a Spirocompound as Clean Viscosity-Reducer for Crude Oil. *Journal of Chemistry*. **5**, (2016).

17. Deshmukh, S., Bharambe, D. P., Wax Dispersant Additives for Improving the Low Temperature Flow Behavior of Waxy Crude Oil,Energy Sources, Part A: Recovery, Utilization, and Environmental Effects. *Energy Sources. Part A,* **34,** 1121–1129 (2012).

18. Chen, G., Li, Y., Zhao, W., Qu, K., Ning, Y., Zhang, J., Investigation of cyclohexanone pentaerythritol ketal as a clean flow improver for crude oil. *Fuel Processing Technology*. **133**, 64-68 (2015).

19. Chang, C., Boger, D.V., and Nguyen, Q.D., The yielding of waxy crude oils. *Ind. Eng. Chem. Res.* **37**, 1551-1559 (1998).

20. CORMA, A., MART~N-ARANDA, R. M., and SANCHEZ., Zeolites as Base Catalysts: Condensation of Benzaldehyde Derivatives with Activated Methylenic Compounds on Germanium-Substituted Faujasite. *Journal of Catalysis.* **126,** 192-198 (1990).

21. Al-Sabagh, A. M., Betiha, M. A., Osman, D. I., Hashim, A. I., El-Sukkary, M. M., Mahmoud, T., Synthesis and Characterization of nanohybrid poly(Octadecylacrylat derivatives) / montmorillonite as pour point depressant & flow improver for waxy crude oil. *Journal of Applied Polymer Science.* DOI: 10.1002/A, 47333 (2018).

22. Al-Sabagh, A. M., Abdel_Hai, F., Abd El Rhman, A. M., EL-Shafie, M. M., Mohammedy, M. M., Studies on the efficiently of some polymers based on octadecyl acrylate as crude oil additives. *Life Science Journal*. **11**(11s), (2014).

23. Al-Sabagh, A. M., Betiha, M. A., Osman, D. I., Hashim, A. I., El-Sukkary, M. M., Mahmoud, T., Preparation and Evaluation of Poly(methyl methacrylate)- Graphene Oxide Nanohybrid Polymers as Pour Point Depressants and Flow Improvers for Waxy Crude Oil. *Energy & Fuels, Energy Fuels.* **30** (9), 7610–7621 (2016).

24. Mahto, V., Singh, H., Effect OF Temperature and Pour Point Depressant on The Rheology of Indian Waxy Crude Oil. *International Journal of General Engineering and Technology (IJGET).* **4**(2), 2530 (2013).