IOSR Journal of Engineering (IOSRJEN) **www.iosrjen.org**
ISSN (e): 2250-3021, ISSN (p): 2278-8719
Vol. 12, Issue 7, July 2022, ||Series -I|| PP 48-52

Performance Dependence of Pour Point Depressants on Solvents

E. O.Ohimor[1*] and A. P.Ekwealor[2]
[1,2]Department of Chemical Engineering, Federal University of Petroleum Resources, Effurun, Delta State, Nigeria
Corresponding Author: Ohimor E. O.

Received 08 July 2022; Accepted 25 July 2022

ABSTRACT
This study is on the performance analysis of different chemical compounds in various solvent as pour point depressants (PPD) for crude oil. Triethanolamine and Polymethacrylate were the chemical components, while the solvents were Dual Purpose Kerosene (DPK), Automotive Gas Oil (AGO) and Ethanol. The chemical compounds and the solvents used as PPDs were in the ratio of 1:10. The experiment was carried out in accordance with ASTM D97 using a SETA cloud and pour point refrigerator. Pour points of the crude before and after treating with a pour point depressant were obtained and recorded. The pour point depressant tagged A3, displayed a poor flow improving capability with a pour point reduction value of 3°C owing to chemistry of hybridized shell of the polymer. The analysis of Polymethacrylate + DPK and Polymethacrylate + AGO tagged, A2 and A1 showed relatively good effect on the pour point of the crude oil samples with a corresponding depression value of 28°C and 25°C respectively. The pour point depressant containing Triethanolamine + Ethanol tagged B3, gave an excellent result in the pour point depression of the crude oil with a value of 31°C. This indicates that, Triethanolamine + Ethanol tagged B3, is a good pour point depressant and crude oil flow improver.

Keywords: Paraffins, Triethanolamine, Polymethacrylate, Crude oil, Flow Assurance

I. INTRODUCTION

Crude oils are complex hydrocarbon mixtures containing non-polar n-paraffins and polar components such as asphaltenes. Crude oil composition varies geographically, as well. Operators of petroleum production processes often encounter problems related to flow assurance. The discipline of Flow Assurance denotes the branch of knowledge associated with designing production systems for continuous, safe and uninterrupted transport of crude oil from reservoirs to processing facilities. Major challenges associated with ensuring flow of crude oil include solid deposition such as wax (parrafins), asphaltenes, scale, naphthenates and gas hydrates lines [1]. Paraffin deposition in trunk lines and transmission lines exposed to cooler climatic conditions increases the overall cost of getting oil to the market [2]. For instance, in Nigeria, pipelines have been known to wax up beyond recovery [3]. Also, production tubing has been known to wax up (e.g. Agip) necessitating frequent wax cutting, which is expensive [4]. In 2007, 1500bpd was deferred due to wells closed in as a result of wax problems in one the crude oil fields in the Niger Delta region of Nigeria [5]. In a particular case, the wax deposition was so severe and frequent that an off-shore platform in the North Sea (Lasmo field in UK) had to be abandoned at a cost of about $100,000,000 [6]. Gelled pipeline shut-in and restart in a serious flow assurance problem currently faced in the petroleum transport industry [7]. In the worst cases, production must be stopped in order to replace the plugged portion of the pipeline. The cost of this replacement and downtime is estimated approximately at $30,000,000 per incident [8].

Waxes, also referred to as paraffins are high molecular weight saturated aliphatic components of crude oil with carbon chain length varying from 16 to about 100. Asphaltenes are polynuclear aromatic hydrocarbon molecules in which non-aromatic aliphatic chains are also present along with heteroatoms. At reservoir temperatures (above 70°C) and pressures (above 50MPa), wax molecules usually dissolve in the crude oil. However, as the crude oil flows through subsea pipeline at a temperature as low as 4°C, due to heat losses to the surroundings the temperature of oil eventually decreases below its Cloud Point and Wax Appearance Temperature. The solubility of wax decreases with decrease in temperature and wax molecules starts to precipitate out of the crude oil.

From the foregoing, it is clear that the dissolution of wax or prevention of wax deposition is one key aspect of flow assurance [9]. Pour point depressants (PPD) are critical components of crude oil treatment programs that prevent wax crystals in the crude oil from forming large crystal networks which can inhibit flow at cold temperatures. Many of these problems can be effectively resolved by the appropriate application of pour point depressing chemicals. Crude oil pour point depressant is significant in eliminating paraffin wax deposition [3] and is crucial for control of flow behavior, transportation and storage of crude oil.

The paper is aimed at carrying out a comparative study of the performance of crude oil pour point depressants, having the active compounds, dissolved in selected solvents, in order to select an appropriate pour point depressant for a waxy crude oil in Nigeria.

II. MATERIALS AND METHODS

Materials

The materials used are; untreated crude oil emulsion, PPD active compounds (Triethanolamine and Polymethacrylate), solvents such as Dual-Purpose Kerosene (DPK), Automotive Gas Oil (AGO) and Ethanol, Hydrometer, SETA Cloud and Pour Point Cabinet, Water bath, Thermometer, Volumetric cylinders, Beaker, Micropipettes, Sample bottles.

The crude oil used in this experiment was obtained from the Petroleum Training Institute (PTI) Laboratory in Warri, Delta State. The physicochemical properties of the crude oil were determined. The active components and solvents were bought from chemical vendors in Warri, Delta State.

Preparation of the Pour Point Depressants (PPDs)

The pour point depressants were made by blending the active components and any of the solvents in ratio of 1:10 by volume. The pour points depressants were subsequently used in treating the crude oil at different dosage in part per million (ppm) (1,000ppm – 10,000ppm) and their effect on the pour point of the crude oil were obtained.

Determination of the Pour Point

The experiment was carried out in accordance with the ASTM D97 procedure[10].

The crude oil was reconditioned (heated) to about a temperature of 50°C to erase any previous history that might exist in such sample. Reconditioning the sample ensured that all pre-crystallized wax got dissolved into the crude oil, thereby erasing any thermal and shear history and producing homogenous sample for testing.

After preliminary heating, the sample was cooled at a specified rate and examined at intervals of 3°C for flow characteristics. The lowest temperature at which movement of the specimen is observed is recorded as the pour point. Pour the specimen into the test jar to the level mark. When necessary, heat the specimen in a water bath until it is just sufficiently fluid to pour into the test jar. Closed the test jar with the cork carrying the high-pour thermometer.

Remove the high cloud and pour thermometer, and place the low cloud and pour thermometer in position. After seeing that the disk, gasket, and the inside of the jacket were clean and dry, the disk was placed in the bottom of the jacket. The gasket was placed around the test jar, 25 mm from the bottom. Insert the test jar in the jacket. After the specimen has cooled enough, to allow the formation of paraffin wax crystals, take great care not to disturb the mass of specimen nor permit the thermometer to shift in the specimen, any disturbance of the spongy network of wax crystals will lead to low and erroneous results.

Pour points were expressed in integers that are positive or negative multiples of 3°C. Begin to examine the appearance of the specimen when the temperature of the specimen is 9°C above the expected pour point (estimated as a multiple of 3°C). At each test thermometer reading that is a multiple of 3°C below the starting temperature the test jar was removed from the jacket. Condensed moisture that limits visibility was wiped from the surface with a clean cloth moistened in alcohol (ethanol or methanol). Tilt the jar just enough to ascertain whether there is a movement of the specimen in the test jar The complete operation of removal, wiping, and replacement were carried out in not more than 3 seconds.

If it was observed that the specimen in the jar no longer flows when tilted, then hold the jar in a horizontal position for 5 seconds, using an accurate timing device and observe carefully. As soon as the specimen shows some movements, return the test jar immediately to the jacket and repeat the test for flow at the next temperature, 3°C lower.

Continue in this manner until a point is reached in which the specimen shows no movement, when the test jar is held in a horizontal position for 5 seconds. Record the observed reading on the test thermometer.

All the above procedures were carried out both on the blank crude and the crude containing the pour point depressants at a temperature of 25°C.

III.RESULTS AND DISCUSSION

Table 1: Physical Appearance of the PPDs

Product Code	Pour Point Depressants	Physical Appearance
Al	Polymethacrylate + AGO	Brownish yellow homogenous mixture
A2	Polymethacrylate + DPK	Colourless homogenous mixture
A3	Polymethacrylate + Ethanol	Heterogenous solution (precipitate particles)
B1	Triethanolamine + AGO	Immiscible
B2	Triethanolamine + DPK	Immiscible
B3	Triethanolamine + Ethanol	Colorless homogenous mixture

The mixture of polymethacrylate and ethanol showed a slight dissolution and observed precipitated particles on the surface. This may be as a result of the presence of hydration shells around the carbonyl group of the polymer, which acts as a compatibilizing layer between the polymer and ethanol. Also, the triethanolamine was completely immiscible with DPK and AGO, because a clear separation between both liquids was observed. This is because triethanolamine is a polar compound due to the geometry of the molecules, whereas DPK and AGO are both non-polar solvents; therefore, triethanolamine cannot be dispersed in either solvents.

Table 2: Properties of crude oil emulsion sample used in the study

Parameters	Values
pH (mg/l)	6.58
Pour point (^{o}C)	19
Specific Gravity	0.84
API	37
Water Cut Range (%)	40

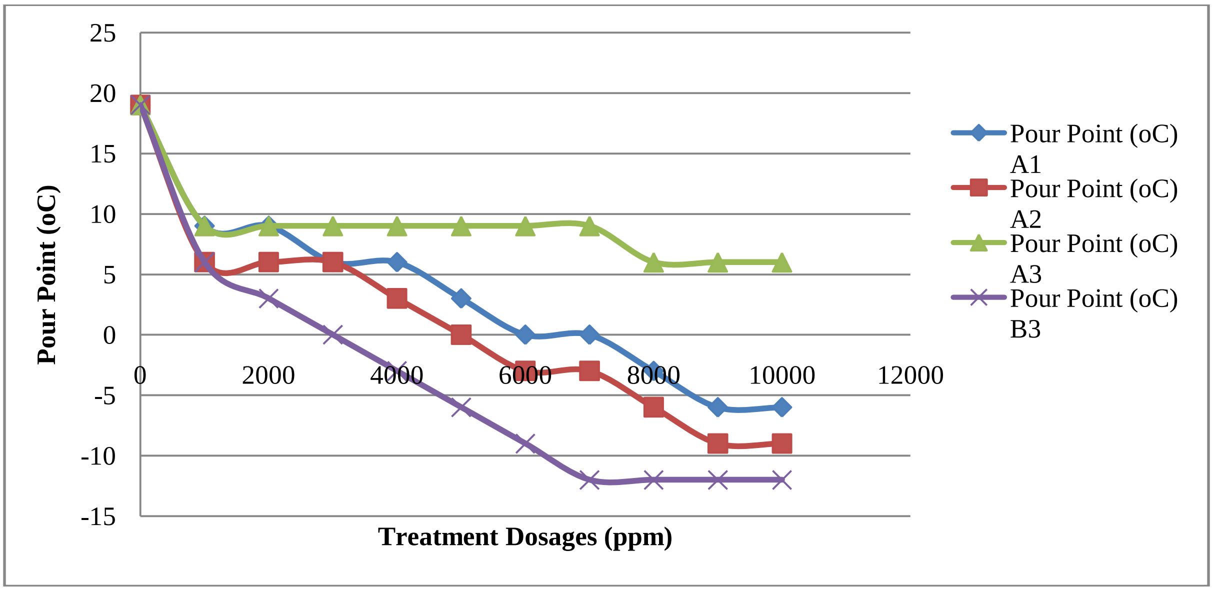

Figure 1: A Graph of Pour Point against Treatment Dosage

The result in Figure 1 shows a uniform decrease in the pour point of the crude oil from 9°C to -6°C, following treatment with pour point depressant, A1 (Polymethacrylate + AGO). A clear reduction in the pour point of the crude oil was observed until a point where further additions of the PPD, A1 no longer have any effect. This showed a decrease of 25°C in the pour point of the crude oil. The graph indicates that the performance of the PPD, A1 in improving the flow of the crude is directly related to the concentration of the active component.

Also, a remarkable effect on the pour point if the crude oil was observed on treating with pour point depressant, A2 (Polymethacrylate + DPK); it was able to reduce the pour point of the crude from 19°C to -9°C, which is 28°C reduction.

Upon treatment of the crude oil with pour point depressant, A3 (Polymethacrylate + Ethanol), it was observed that there was no reduction in the pour point of the crude oil until 8,000ppm and only 3°C reduction. This is an indication of the poor impact of this PPD on the flow performance of the waxy crude oil emulsion. The insignificant reduction in the pour point of the crude implies that PPD, A3 is not effective in preventing the formation of wax networks in the crude oil.

The pour point depressants, B1 and B2 had no results, because Triethanolamine is insoluble in both Diesel and Kerosene respectively. There was a clear liquid-liquid interface; this is as a result of different polarities.

However, the pour point depressant, B3 (Triethanolamine + Ethanol) was able to significantly reduce the pour point of the crude oil from 19°C to -12°C, which is 31°C reduction. This indicates the effectiveness of this PPD, B3 in inhibiting the waxy network formation, thus, signifies a great flow performance. An increasing treatment dosage yields an equivalent increase in the pour point value. However, a diagonal linear relationship was observed till 7,000pppm, where there is no more change in the pour point of the crude irrespective of the amount of PPD dosed.Triethanolamine has been reported [11] to have interference in the wax crystallization process by modifying the crystal structure of the paraffin present in the crude oil resulting in lowering the pour point and viscosity of the crude oil.

It is worthy to note that the efficiency of specific paraffin inhibitor or pour point depressant products is strongly correlated to crude oil composition [12] [13] and PPDs are very selective of crude oil [14].

IV.CONCLUSION

In this study, a comparative analysis of different PPD blends, of Triethanolamine and Polymethacrylate as the active components blended with solvents (AGO, DPK and Ethanol); on waxy crude oil pour point was done in accordance with ASTM D97.

The following conclusions can be drawn from this work;

Pour point of crude can be affected by certain additives, depending on the addictive as well as the solvent.

PPD A3 containing Polymethacrylate+ Ethanol displayed a poor flow improving capability with a pour point reduction value of 3°C owing to chemistry of hybridized shell of the polymer. Polymethacrylate + DPK and Polymethacrylate + AGO showed a relatively good effect on the pour point of the crude sample with a corresponding depression of 28°C and 25°C respectively.

PPD, B3 gave an excellent result in the flow improvement of the crude, having a pour point reduction value of 31°C. This indicates that, Triethanolamine + ethanol is the best flow improver out of all the pour point depressants utilized in this research.

This study investigated the compatibility of two active component (PMA and TEA) with solvents such as AGO, DPK and Ethanol in terms of their effectiveness as PPD at ambient temperature. For further studies and to achieve a better result, the following recommendations may be considered;

The experiment should be carried out at other temperatures other than ambient.

Research should be carried out with different types of crude oil.

REFERENCES

[1]. Kelland, A M, (2009) Production Chemicals for Oil and Gas Industry. S.l, CRC Press

[2]. Koshel, KC & Kapoor, S. (1999) 'Effect of Flow Improver on Indian Wester Offshore Crudecarrying Pipeline A Case Study. SPE Annual Conference and Exhibition

[3]. Adewusi, V A, (1997) Prediction of Was Deposition Potential of Hydrocarbon Systems From Viscosity Pressure Correlation Elsevier Fuel Journal, 76(12), pp. 1079-1083

[4]. Ajienka, A. & lkoku, C, (1990) Waxy Crude Oil Handling in Nigeria Practices, Problems and Energy Sources, 12(4). pp. 463-478

[5]. Sulaimon, A. A & Falade, J. K. (2010). A Proactive Approach for Predicting and Preventing Wax Deposition in Production Tubing Strings, Journal of Petroleum and Gas Engineering. 1(2), pp. 26-36

[6]. Singh, P., Venkatesan, R. & Fogler, H SaN NR. (2000) Formation and Aging of Incipient Thin Film Wax-Oil Gels American Institute of Chemical Engineers Journal, Volume 46, p. 1059

[7]. Jorda, R M, (1996) Paraffin Deposition and Prevention in Oil and Gas Industry SPE Journal of Petroleum Technology. Volume 18, pp 1605-1612

[8]. Venkatesan, R. & Creek, J. L. (2007) Wax Deposition During Production Operations SOTA Houston, Texas, Paper OTC 18798 Presented at 2007 Offshore Technology Conference

[9]. Coutinho, J A & Pauly, Ja D I L (2001) A Thermodynamic Model to Prodia Was Formation in Petroleum Flaids Bracilian Journal of Chemical Engineering 1746), pp: 411-422

[10]. Hansen, A B., Larsen, E. & Pedersen, W. B. (1991) Wax Precipitation from North Ses Crude Oils Precipitation and Dissolution of Wax Studied by Differential Scanning Calorimeter Energy and Fuels, Volume 5, pp 914-923

[11]. Caleb, A, Jerome, A., Olajide, E. & Ogungbe, A, (2015). Triethanolamine (TEA) as Flow Improver for Heavy Crude Oils Journal of Applied Chemistry, Volume 6, pp. 34-38

[12]. Carmen, G, (2003) Effect of crude oil composition and blending on flow properties. Volume 3-6, pp. 863-878

[13]. Mendell, J.L & Jessen, F. W. (1970). Mechanism of Inhibition of paraffin deposition in crude oil system. Paper presented at the SPE production Techniques Symposium, Wichita Falls, Texas.

[14]. Wang, K-S. Wu, C-H & Creek, J. (2003) 'Evalution of effects of selected wax inhibitors on wax appearance and disappearance temperature Petroleum science and technology 21, Volume 3-4, pp 359-368

E. O.Ohimor, et. al. " Performance Dependence of Pour Point Depressants on Solvents." *IOSR Journal of Engineering (IOSRJEN)*, 12(7), 2022, pp. 48-52.