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Experimental Study on the Effect of Inhibitors on Wax Deposition

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Abstract

A challenge facing offshore oil production is wax deposition. It leads to increases in operational and remedial costs while suppressing oil production. Wax inhibitors are one of the mitigation technologies that had been examined its influence on crude oil viscosity, pour point and wax appearance temperature (WAT).

The performance of some of wax inhibitors was evaluated to determine their effects on the pour point, wax appearance temperature and the viscosity of the crude oil using the programmable Rheometer rig at gradient temperatures (55°C) and shear rate 120 1/s before and after adding 1000 ppm and 2000 ppm of inhibitors to the crude oil. Three different inhibitors which were not tested before were prepared in the lab of this study. These inhibitors works well compared with its original components.

The first inhibitor was coded Mix01 by mixing polyacrylate polymer (C16-C22), and copolymer + acrylated monomers. The reduction of pour point of the waxy crude oil was up to a 16.6ºC at 2000 ppm concentration and this reduces the crude oil viscosity to about 61.9% at a seabed temperature of 4ºC.

The second inhibitor was coded Mix02, by mixing polyacrylate polymer (C16-C22), alkylated phenol in heavy aromatic naphtha, and copolymer dissolved in solvent naphtha. At 2000 ppm, the reduction of pour point of the crude oil up to a 15.9ºC and decreases the viscosity to 57% at a seabed temperature of 4ºC. Finally, the third inhibitor was Mix03, by mixing polyacrylate polymer (C16-C22), and brine (H_2O + NaCl). At 1000 ppm concentration, the reduction of pour point of the oil was up to a 14.4ºC and reduced the viscosity to 52.5% at a seabed temperature of 4ºC.

This unique blend of the inhibitory properties and significant reduction in pour point temperatures and crude oil viscosity is providing an original development in wax mitigation technology.

Keywords: Inhibitors; Wax; Oil; Phenol; Viscosity; Crystallization

Introduction

Paraffin wax deposition is a phenomenon that plagues the oil industry. It can choke the production lines thereby reducing the oil production to uneconomic levels. Wax inhibitor, alternatively known as pour point depressant/ wax crystal modifier, can reduce the growth of the wax crystal and form smaller crystals allowing large free space of the liquid fraction of the crude oil to flow freely [1].

The chemical addition is one of the inhibitors that have been used to reduce or prevent wax deposition in crude oil production. These inhibitors can be divided into four types: pour point depressants (PPD), crystal modifiers, dispersants, and solvents. PPD hinders the formation and growth of wax crystals by modifying the crystal structure (by merging with the edge of a growing wax crystal). Although it reduces the viscosity, yield stress, and pour point of oil, it cannot reduce the wax deposition rate [1].

The crystal modifier has a similar molecular structure to wax. It co-precipitates or co-crystallizes with a wax crystal by replacing wax molecules on the crystal lattices. It imposes steric hindrance on paraffin crystals that interfere with the proper alignment of the new incoming paraffin molecules such that growth terminates. Typical crystal modifiers are polyethylene, copolymer esters, ethylene/vinyl acetate copolymers, olefin/ester copolymers, ester/vinyl acetate copolymers, polyacrylates, polymethacrylates, and alkyl phenol resins. Dispersants are similar to surfactants in their molecular structure. Dispersants are breaking wax crystals up into much smaller particles and reduce the rate of wax deposition and prevent it by minimizing wax adhesion to the pipe wall [1,2].

Solvents increase the solubility of wax in oil and so dissolve already deposited wax. The solvents most commonly used today include aromatic compounds (toluene, and xylene), white or unleaded gasoline, and pine-derived terpenes [1].

The advantage of the wax inhibitor addition to the crude oil sample is the deposition can be mitigated without stopping production. Even though many wax inhibitors have been developed, there is currently no universal type can be used for all types of crude oils due to the varying properties of the crude oils [1,3].

Hoffmann and Amundsen [4] found that about 60% to 90% of wax thickness was reduced by applying different inhibitor concentration during experimental work investigation. The presence of the small amount of inhibitor concentration such as poly (ethylene-co-vinyl acetate (EVA)) and poly (maleic anhydride-alt-1-octadecene (MA)), can coalesce with wax crystals and interfere the crystal growth of the crystals [5].

Polymers have been used successfully as crystal modifiers in some areas; their use should expand as more effective polymers are developed. The polymers molecular weight also has influence on the pour point depression. Short or lower molecular weight polymers may

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cause little disruption to the wax crystal agglomeration and growth, while very long and high molecular weight polymers can interact within the molecule itself instead of with the wax structures. This interaction reduces the rate of wax formation, leading to formation of softer wax that is easy to transport [6,7]. The reduction in the pour point and the crude oil viscosity had been making the transportation of the crude oil easier [8,9].

All the inhibitors have been used in the current work are based on polymers which are normally used as pour point depressants/crystal modifiers such as Alkylated phenol in Heavy Aromatic Naptha (HAN), Polyacrylate based polymer (C16-C22), Copolymer + acrylated monomers, Co-polymer dissolved in solvent naphtha and three inhibitors, which were not tested before were prepared by mixing some of the previous inhibitors as will illustrated in the methodology.

Methodology

Regarding to study the effects of inhibitors on wax deposition that have been used in this study, the crude oil was heated to 60°C using hot bath water for one hour to dissolve all wax crystals present in the oil and to bring the crude up to a suitable temperature for treatment. A Bohlin Gemini II Rheometer (Figure 1) was used to measure the viscosity, pour point and wax appearance temperature of the crude oil.

Treated samples

- The crude oil should be maintained at a temperature approximately 20°C above the wax appearance temperature in a hot water bath for 1 hour before commencing the test work.
- Measure 40 ml of crude oil into a test tube then dose with the required inhibitor at concentration 1000 ppm and 2000 ppm or leave undosed to act as a blank.
- Stirring the mixture for few minutes at 60°C to make sure of the reaction and to increase the influence of the inhibitor on wax crystals.

Viscosity/temperature profile

- A Bohlin Gemini II Rheometer was used to measure the viscosity of the crude oil with and without inhibitors at a cooling range from 55°C down to 0°C at a rate of 5°C/min and shear rate of 120 1/s.
- The data for the dosed samples should then be compared to the blank results, and the chemical that maintains the flattest, smoothest trace for the longest time is considered the most effective wax inhibitor.

Pour point

A Bohlin Gemini II Rheometer was used to measure the pour point of the crude oil with and without inhibitors. It was determined from the elbow point in the viscosity curve of the crude oil, where at which the liquid converted from non-Newtonian to a Newtonian liquid as shown in Figure 2.

Wax appearance temperature (WAT)

WAT is the temperature at which the first wax crystals start to form and precipitate, from crude oil, on the cold surface of the pipe [10]. The rheometer was used to measure the viscosity of the crude oil at shear rate 120 1/s and different temperatures. The WAT was determined from the converted point in the viscosity curve from the straight line to the incline line, at which the viscosity start to increase gradually when the temperature is decreased, as shown in Figure 3.

Preparing the new inhibitors

Three wax inhibitors, which were not tested before were prepared in the lab of this work to study its effects on wax deposition and compare the results with original components. The first one coded Mix01 by mixing 33% of each of W802, W804 and W805 (Table 1), at 70ºC to increase the reaction between the mixtures (Table 1).

The second inhibitor Mix02 was developed by mixing 33% of each of W802, W302 and W510. Finally, the third inhibitor settled in this subject was Mix03 by mixing 50% of W802 and 50% of brine (H_2O + NaCl).

Results and Discussion

Effect of inhibitors on viscosity

The performance of some of wax inhibitors was evaluated to determine their effects on the wax precipitation. The effect was on the pour point, wax appearance temperature and the viscosity of the crude oil.

The analysis of the crude oil viscosity with the inhibitors shows that the new mixtures Mix01 and Mix02 produced the greatest reduction

Figure 1: A Bohlin Gemini II Rheometer was used to determine pour point, viscosity and WAT of the crude oil before and after adding the inhibitors.

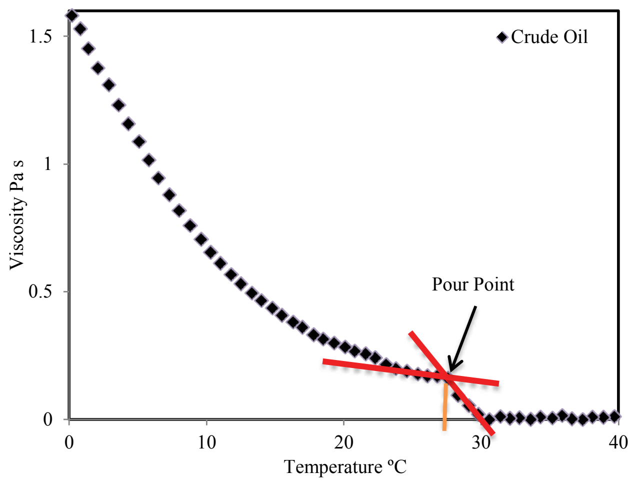

Figure 2: Determine the pour point from the viscosity curve of the crude oil using the rheometer.

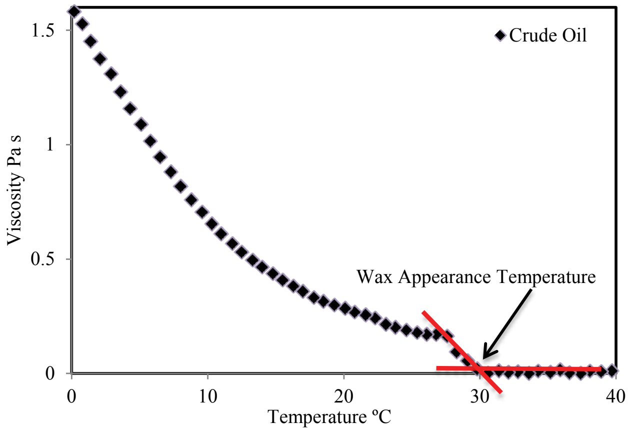

Figure 3: Determine the wax appearance temperature from the viscosity curve of the crude oil using the Rheometer.

Inhibitor Code	Inhibitor Chemistry
W302	Alkylated phenol in Heavy Aromatic Naptha (HAN).
W802	Polyacrylate based polymer (C16-C22).
W804	Copolymer + acrylated monomers.
W805	Copolymer + acrylated monomers.
W510	Co-polymer dissolved in solvent naphtha.
Mix01 (New)	Polyacrylate based polymer (C16-C22) + copolymer + acrylated monomers.
Mix02 (New)	Polyacrylate based polymer (C16-C22) + Alkylated phenol in Heavy Aromatic Naptha (HAN) + Co-polymer dissolved in solvent naptha.
Mix03 (New)	Polyacrylate based polymer (C16-C22) + Brine (H_2O + NaCl).

Table 1: The chemistry of wax inhibitors has been used during this study.

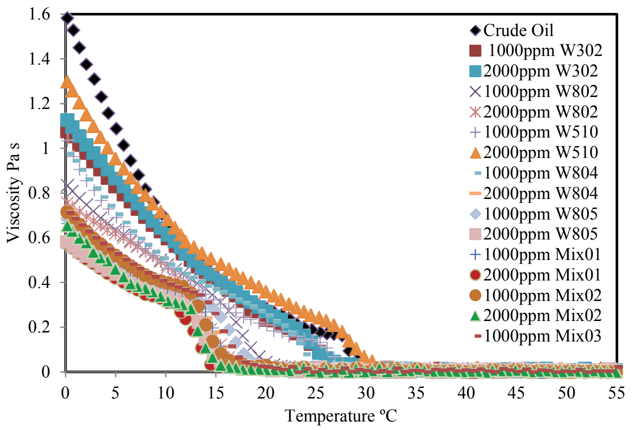

Figure 4: The effect of inhibitors on viscosity at different temperatures.

in viscosity at concentration 2000 ppm comparing with its original components at the same concentration, see Figure 4. The products were all tested at 1000 ppm and 2000 ppm.

The prepared mixtures were produced better result compared with its original components, due to increase the monomers in the mixture and that means increase the ability to prevent wax crystal formation. The first inhibitor Mix01 at 2000 ppm was reduced the crude oil viscosity up to 61.9% at seabed temperature of 4°C, as shown in Figure 5. The second inhibitor Mix02 at 2000 ppm concentration was decreased the viscosity up to 57% at seabed temperature of 4°C, as shown in Figure 6. Finally, the third inhibitor Mix03 at 1000 ppm concentration was reduced the viscosity up to 52.5% at seabed temperature of 4°C, as shown in Figure 7.

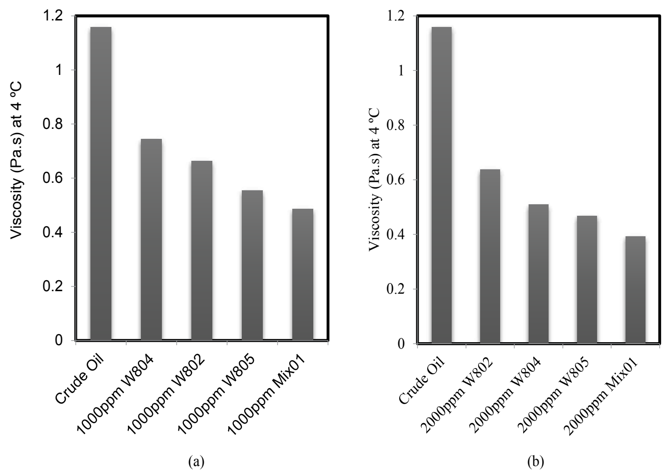

Figure 5: The effect of Mix01 and its components on crude oil viscosity at 4°C, (a) 1000 ppm (b) 2000 ppm.

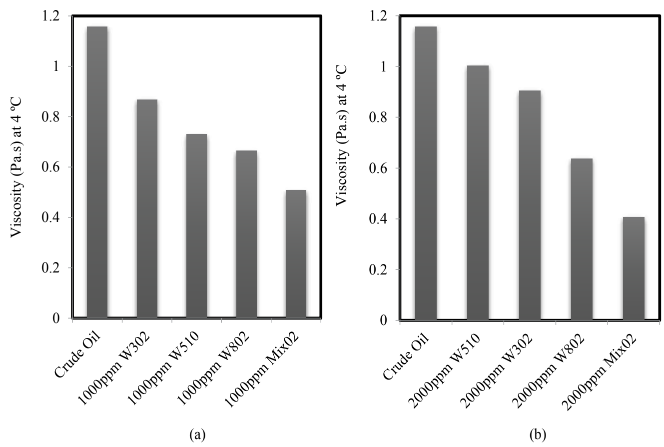

Figure 6: The effect of Mix02 and its components on crude oil viscosity at 4°C, (a) 1000 ppm (b) 2000 ppm.

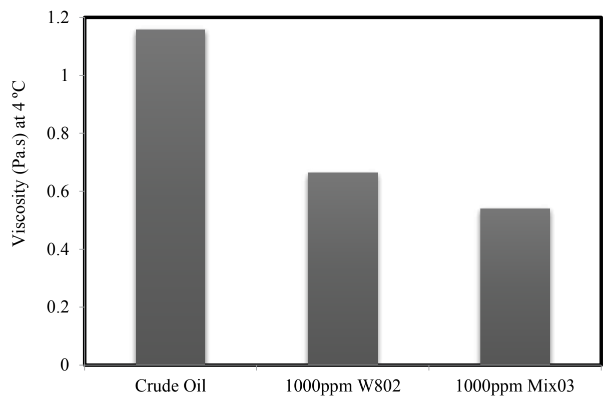

Figure 7: The effect of Mix03 and its components on crude oil viscosity at 4°C and concentration 1000 ppm.

Effect of inhibitors on pour point

The pour point is the temperature at which it becomes semi solid and loses its flow characteristics. The first inhibitor Mix01 was reduced the pour point of the waxy crude oil from 27.6°C to 11°C at 2000 ppm concentration, as shown in Figures 8 and 9. The second inhibitor Mix02 at 2000 ppm concentration was produced better result compared with its components, where it decreased the pour point of the crude oil from 27.6°C to 11.7°C, as shown in Figure 10. Finally, the third inhibitor Mix03 at 1000 ppm concentration was reduced the pour point of the oil from 27.6°C to 13.2°C, as shown in Figure 11.

Effect of inhibitors on wax appearance temperature

The wax appearance temperature of the crude oil has been reduced by adding the new inhibitors of this study, where it is decreased up to 52% by adding the new inhibitor Mix01 and up to 48.3% by adding Mix02 at concentration 2000 ppm respectively; and up to 41% by adding the inhibitor Mix03 at concentration 1000 ppm as shown in Figures 12, 13 and 14 respectively.

This can be interpreted as by increasing the concentration of Mix01 from 1000 to 2000 ppm the quantity of the polyacrylate polymer and the acrylated monomers will be increased, providing more structures to interfere and merge with the edge of a growing wax crystal.

The reduction in WAT and viscosity due to add Mix02 can be explained as by increasing the concentration of polyacrylate polymer, alkylated phenol and co-polymer dissolved in naphtha, the wax crystals will be decreased due to increase the molecules that prevent wax crystal formation and preserve it in smaller particles.

The third Mix03 contain of mixing polyacrylate polymer and brine (H_2O + NaCl) and this will lead to producing sodium polyacrylate and this will absorb and merge with the wax crystals and prevent it to combine together.

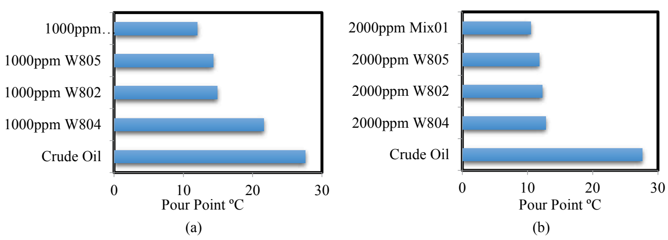

Figure 8: The effect of Mix01 and its components on pour point Temperature (a) 1000 ppm and (b) 2000 ppm.

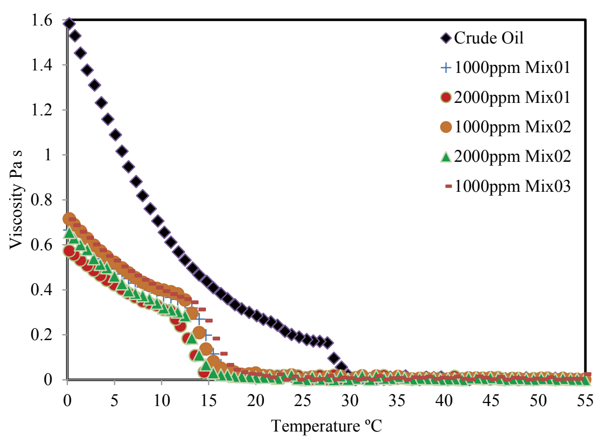

Figure 9: Comparison between the new mixtures Mix01, Mix02 at 1000 ppm and 2000 ppm, and Mix03 at 1000 ppm as shown in Figure 8.

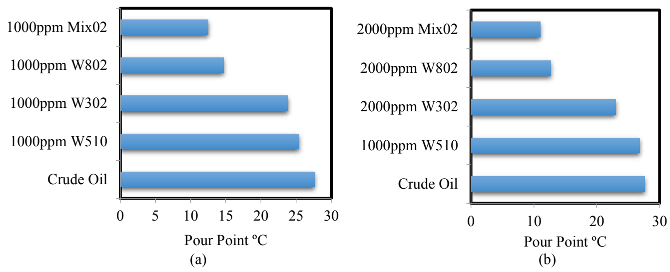

Figure 10: The effect of Mix02 and its components on pour point Temperature (a) 1000 ppm and (b) 2000 ppm.

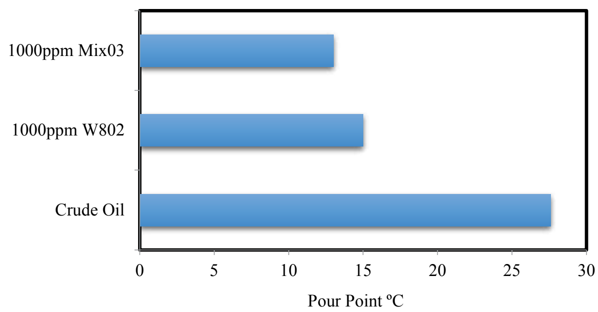

Figure 11: The effect of Mix03 and its components on pour point temperature at concentration 1000 ppm.

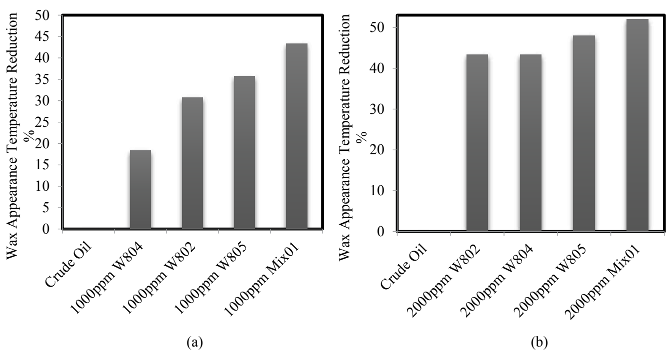

Figure 12: The effect of Mix01 and its components on WAT (a) 1000 ppm and (b) 2000 ppm.

Comparison between the prepared mixtures

From Figures 8 and 9, it was noticed that at concentration 1000 ppm that Mix02 was produced better results, compared with Mix01 and Mix03, in pour point and wax appearance temperature 12.5°C and 16.3°C, respectively. At 2000 ppm Mix01 was produced best results compared with the prepared mixtures and the original inhibitors, where it was the pour point and the wax appearance temperature 11°C and 14.5°C , respectively.

These inhibitors (Mixtures) at concentration 1000 ppm and 2000 ppm improved the reduction in wax crystal formation by interfering with wax crystallization and prevent growth process. However, this interfering mechanism has not yet been fully understood [11]. The

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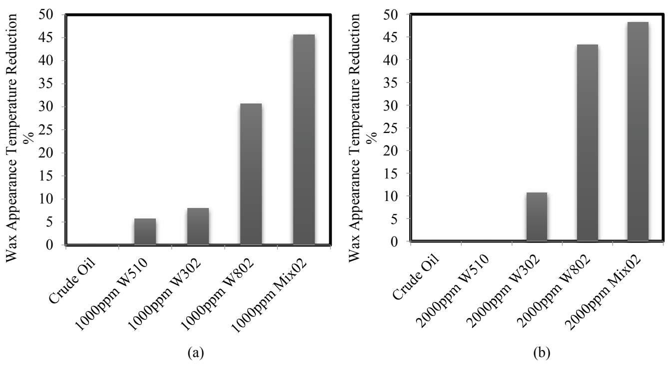

Figure 13: The effect of Mix02 and its components on WAT (a) 1000 ppm and (b) 2000 ppm.

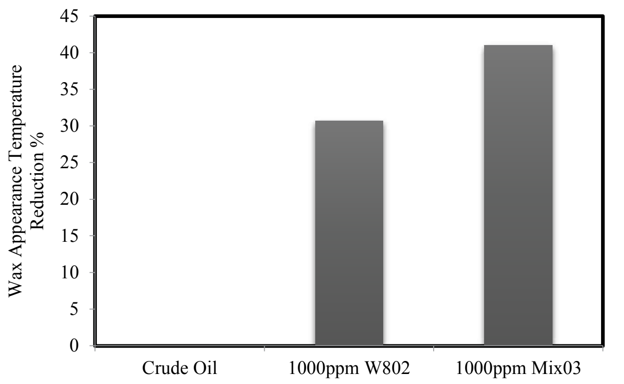

Figure 14: The effect of Mix03 and its components on WAT of the crude oil at 1000 ppm.

major theory stated the possibility of wax inhibitor polymers containing similar structure to the wax structure, thereby allowing the inhibitor crystal to be incorporated into the wax crystal growth. Sometimes the structural part of the polymer covers the wax site, thereby preventing further wax crystal growth and promoting the formation of smaller wax aggregates [9,11].

Conclusion

Wax deposition in offshore pipelines and other production equipment can pose significant flow problems requiring remediation. Wax inhibitors are considered one of the suitable mitigation technologies in the deep water because it does not need to stop production.

The performance of some of wax inhibitors was evaluated to determine their effects on the pour point, wax appearance temperature and the viscosity of the crude oil using the programmable Rheometer rig at gradient temperatures (55°C) and shear rate 120 1/s before and after adding 1000 ppm and 2000 ppm of inhibitors to the crude oil.

During this research, three different inhibitors were prepared, these inhibitors works more efficient compared with its original components. The first inhibitor was coded Mix01 by mixing 33% of each of polyacrylate polymer (C16-C22), and copolymer + acrylated monomers. The reduction of pour point of the waxy crude oil was from 27.6°C to 11°C at 2000 ppm concentration of Mix01 and this reduces the crude oil viscosity to about 61.9% at a seabed temperature of 4°C.

The second inhibitor was coded Mix02, by mixing 33% of each of polyacrylate polymer (C16-C22), alkylated phenol in heavy aromatic naphtha, and copolymer dissolved in solvent naphtha. At 2000 ppm, the reduction of pour point of the crude oil from 27.6°C to 11.7°C and decreases the viscosity to 57% at a seabed temperature of 4°C. Finally, the third inhibitor was Mix03, by mixing 50% of each of polyacrylate polymer (C16-C22), and brine (H_2O+NaCl). At 1000 ppm concentration, the pour point of crude oil was reduced from 27.6°C to 13.2°C and reduced the viscosity to 52.5% at a seabed temperature of 4°C.

A comparison between the prepared mixtures was completed, where it was noticed that at concentration 1000 ppm that Mix02 was produced better results, compared with Mix01 and Mix03, in pour point and wax appearance temperature 12.5°C and 16.3°C, respectively. At 2000 ppm Mix01 was produced best results compared with the prepared mixtures and the original inhibitors, where it was the pour point and the wax appearance temperature 11°C and 14.5°C respectively.

This unique blend of the inhibitory properties and significant reduction in pour point temperatures, wax appearance temperatures and crude oil viscosity is providing a forward step in wax mitigation technology to be study.

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