Available online at www.vurup.sk/petroleum-coal Petroleum & Coal 56(2) 139-142, 2014

EXPERIMENTAL INVESTIGATION OF THE POLYMERIC FLOW IMPROVER ON WAXY OILS

Taraneh Jafari Behbahani

Refining Technology Development Division, Research Institute of Petroleum Industry (RIPI), P.O.Box 14665-1998, Tehran, Iran, jafarit@ripi.ir

Received January 23, 2014, Accepted April 22, 2014

Abstract

A variety of techniques have been used in order to reduce problems caused by the crystallization of paraffin during the production and/or transportation of waxy oils. Flow improvers are used extensively to increase the mobility of waxy oils. In this work, the influence of different concentrations of polymeric flow improver such as dodecyl polymethacrylate and tetradodecyl polymethacrylate on pour point of waxy oils has been investigated. The results show that the polymeric flow improver improves the pour point of the waxy oils, but the relation between pour point decrease and polymeric flow improver concentration is not linear. It was also found that the performance of the polymeric flow improver dissolved in isooctane was better than the effect of pure flow improver. Also, the results indicate that the higher molecular weight flow improver (tetradodecyl polymethacrylate) has better efficiency on pour point of waxy oils.

Key words: polymeric flow improver; pour point; waxy oil.

1. Introduction

Waxy oils are producing in many countries around the world. The presences of waxes in this oils cause serious problems for process. The flow properties of waxy oil are strongly affected by its chemical composition, temperature, pressure condition and previous thermal history. Waxy Oils containing a large amount of wax has high pour point and high viscosities ^[1]. If the waxy oils are allowed to cool, wax will crystallize, agglomerate and entrap the oil into its structure. This phenomenon often happens if the ambient temperature is below the pour point of the waxy oils ^[2]. Wax is the high molecular weight paraffin fraction of crude oil that can be separated with reduction in oil temperature below pour point of oil. The solubility of waxes with high molecular weight decreases by decreasing in temperature. In the cold environment at temperatures below the oil pour point, the temperature gradient in the oil creates a concentration gradient in the dissolved waxes due to their difference in solubility. The types of wax crystal were shown in Figure 1.



Macrocrystalline

Microcrystalline

Crystal Deposite Network of Wax

Figure 1 The types of wax crystals

Pretreatment of the waxy oils is necessary. Pretreatment of the waxy oil with wax inhibitor is a method by which the rheological character of the waxy oils changed for easier transportation ^[3-4]. Wax inhibitor, alternatively known as pour point depressant (PPD)/wax crystal modifier; can reduce the growth of the wax crystal and forms smaller crystals of a higher volume to surface ratio ^[5]. Basically three main groups of chemicals are used:

1 Wax inhibitors or Wax crystals modifiers

- 2 Detergents
- 3 Dispersants

The last two groups are primarily surface- active agents for example polyesters and amine ethoxylates. These may act partly by modifying the surface of the pipe wall, but primarily by keeping the crystals dispersed as separate particles, thereby reducing their tendency to interact and adhere to solid surfaces. Wax inhibitors are substances capable of building into wax crystals and alter the growth and surface characteristics of the crystals.

One effect utilized in waxy oil production is the reduced tendency of the crystals to stick to metallic surfaces. Besides, the wax inhibitors will have the effect of reducing the tendency to form a three- dimensional network, thereby lowering the pour point as well as the viscosity. Hence, the name "pour point depressant" is also used for this class of chemicals ^[6-7]. Mechanism of modifiers on wax is not clearly understood, but it is clear that they enhance crystal morphology. Thereby reducing the tendency of crystals to interlock and form three-dimensional networks. There is certainly a combination of different mechanisms involving nucleation, co crystallization, and adsorption. Different observations have been reported as to whether the wax inhibitors cause larger or smaller crystals, aggregate structures, etc.^[8-9]. Jafari Behbahani *et al.* ^[10-12] studied the relationship between molecular weight of flow improver, asphaltene content and rheological behavior of Iranian waxy crude oil.

Recently the experimental and modeling of precipitation and deposition of heavy cut in Iranian crude oils was investigated by Jafari Behbahani *et al.* ^[13-20] A number of polymeric compounds such as tetradodecylpolymethacrylate are used as wax inhibitor for waxy oils. In this work the effect of polymeric flow improver on waxy oil has been investigated. Two wax inhibitors with different molecular weight were evaluated by studied waxy oil.

2. Materials and methods

2.1. Material

Dodecyl polymethacrylate and tetradodecyl polymethacrylate as wax inhibitor with two different molecular weights were selected.

Waxy oil (pour point =-5°C) was used for evaluating the performance of two wax inhibitors.

2.2. Apparatus and Evaluation tests

An appropriate quantity of wax inhibitor was added to the waxy oil. Pour points were measured by ASTM D-97 method ^[21]. Molecular weights of wax inhibitor were determined by a Waters gel permeation chromatograph, equipped with a refractive index detector and ultrastyragel columns of 10^6 , 10^5 , 10^4 and 500 °A connected in series. Tetrahydrofuran at 1 ml/ min flowrate was used as mobile phase.

3. Results and discussion

3.1. Effect of molecular weight of wax inhibitor on pour point of waxy oil

Table 1 shows influence of the wax inhibitor on the pour points. It can be observed that high molecular weight wax inhibitor shows better efficiency for reduction of pour point of waxy oil.

The crystal growth rate of the lower molecular weight wax inhibitor is much slower than that of the higher molecular weight wax inhibitor. As the crystal growth rate of higher molecular weight flow improver is faster, it cannot co-crystallize with reduced size of wax crystals. This is the reason why higher molecular weight wax inhibitor shows better efficiency for waxy oil.

Туре	Average molecular weight	Concentration (wt.%)	Pour point (°C)
Tetradodecyl		0.5	-29
	10 896 0.75 1	0.75	-34
polymethaciylate		1	-35
Dodecyl polymethacrylate	7 987	0.5	-15
		0.75	-25
		1	-29

Table 1 Effect of different wax inhibitors on the pour point of the waxy oil (Pour point=- 4°C)

Figure 2 shows influence of concentration of the wax inhibitor on the pour points. Results show the relation between pour point and wax inhibitor concentration is not linear.





3.2. Effect of solvent on pour point of waxy oil

Isooctane is good solvent for methacrylates. Effect of waxy oil dilution with different solvent concentration was shown in Table 2. As shown influence of wax inhibitor and solvent concentration was compared.

Table 2 Eff	ect of solvent	on the pour	point of waxy	[,] oil (Pour	point=5°C)
				(

Concentration of solvent (Isooctane)	tetradodecylpolymetha crylate (wt.%)	Pour point of waxy oil(°C)
0	0	-5
0	1	-35
2	1	-38
5	1	-51
8	1	-55
10	1	<-70

Upon addition of 10% solvent, pour point of waxy oil reduced from 5 to less than -70°C. The reduction of pour point by addition of solvent is due to the dissolution of asphaltenes. Of course, the effect of dilution may also play a major role in reducing the viscosity. Probably the viscosity reduction is achieved due to the effect of dilution. This study showed that treatment of waxy oil with wax inhibitor alone is not sufficient. In fact the waxy oil will give lower viscosity after dissolution of waxy oil by solvent and subsequent treatment with wax inhibitor.

4. Conclusion

- Results showed that the addition of wax inhibitors improve the pour point of the waxy oil.
- The relation between pours point decrease and wax inhibitor concentration is not linear.
- It was also found that wax inhibitor dissolved in isoparaffin and paraffin such as isooctane was better than the effect of pure one.
- Higher molecular weight wax inhibitor (tetradodecyl polymethacrylate) showed better efficiency as a flow improver.

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