



## A Review on Various Techniques and Recent Advances in Polymeric Additives to Mitigate Wax Problems in Crude Oil

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### ABSTRACT

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Oil and gas industry has long recognized and is continuing to face wax deposition problems, particularly, as more unconventional crudes are being produced. As time goes by, many techniques have been developed to reduce the cost to solve this challenging issue. Polymeric additives, which falls on chemical treatment categories have been extensively used and studied to improve the flow of the crude oil along the pipeline. Nevertheless, the majority of the polymeric additives have dual functions including the use as pour point depressant. This article reviews the various techniques used to improve the flow of crude oil such as mechanical, chemical and thermal treatment, and the recent advances of using polymeric additives to mitigate the wax problems.

#### Keywords:

Wax inhibitor, shear rate, viscosity, pour point depressants

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## 1. Introduction

Crude oil plays an important role as the energy source for supplying energy around the world. Crude oil is a complex mixture of varying hydrocarbon chains. The mixtures of the carbon and hydrogen chains, however, also contain other elements such as sulphur, nitrogen and oxygen. These elements may react with the hydrocarbons to form other complex molecular structures. The hydrocarbons that are present in crude oil are characterized by three types: paraffins, naphthenes, and aromatics. The major percentage consists of paraffins which are important component to produce fuels such as gasoline and diesel [1].

American Petroleum Institute (API) has classified crude oils into light ( $API > 38$ ), medium ( $38 > API > 29$ ) and heavy ( $29 > API$ ) [2]. The flow behavior of the heavy crude oils is the most complex because of the very high wax content ( $>5\%$ ) in these crude oils. Frigaard *et al.*, [3] reported that 20% of the world petroleum resources are made up of the waxy crude oil. In China, the production of the petroleum products is originated from the heavy or the waxy crude oil which dominates 90% of the total crude oil reserves.

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## 2. Deposition of Wax

Petroleum waxes are generally categorized into two kinds, paraffin wax and microcrystalline wax. Paraffin is mixture of hydrocarbons constituted of linear/normal chains, comprising mainly from 20 to 40 carbon atoms, in addition to alkanes with branched and cyclic chains [4,5]. Heavy straight chain paraffinic waxes are hydrocarbons that contain carbon atom ranging from  $C_{18}$  to  $C_{36}$  while, the microcrystalline waxes are consist of branched and cyclic hydrocarbons where the carbon atoms are ranging from  $C_{30}$  to  $C_{60}$ .

Gelling of wax within the pipelines below the wax appearance temperature (WAT) causes the fluid to act as a non-Newtonian fluid where the viscosity of the crude oil increases as the temperature reaches its pour point and will therefore inhibit the flow of crude oil [6]. On the other hand, when the temperature of the pipelines wall is below the WAT, the formation and deposition of a layer of paraffin molecules will be promoted. This layer can grow over time which will cause the diameter of the pipelines to decrease and therefore constricts the flow of the crude oil. This problem usually arises in the deep-sea environments as the temperature of the water in the subsea can reach as low as  $5^{\circ}\text{C}$  even in warm climate [7].

Wax is an aliphatic and non-polar molecule while asphaltene is an aromatic and polar molecule. Nonetheless, despite of the differences, these two oil constituents are similar in various ways where they have a high molecular weight, associate or aggregate in solutions, and have limited solubility in crude oil [8]. However, the deposition of the organic solid wax is a critical problem faced in the production of the crude oil. Deposition of wax is often observed in the production of the paraffinic oils, or in the offshore operations which involve low temperature environment. The causes for the solid wax to deposit and separate from the crude oil includes the heat release from the gas and the oil to the surrounding, invasion of water and vaporization of shorter chain hydrocarbons [9]. The phenomenon where the heat is all released to the environment will decrease the system temperature below the melting point, in turn causes the wax to crystallize and deposit on the wall of the pipelines and in the reservoir.

The process of wax formation occurs when the temperature is kept below its melting point and the wax particles are being stalled due to less energy roaming around freely. Due to the restriction of the movement of the molecules, the wax molecules are coming closer to form a short-lived cluster called nuclei. The formation of nuclei indicates the onset of wax formation [10]. The wax formation starts from a precipitate that acts as the nuclei to allow crystallization process to begin. The crystallization process consists of two main steps: (a) nucleation and (b) crystal growth [11]. Nucleation stage can be further separated into another two steps: primary nucleation and secondary nucleation. Primary nucleation comprises of spontaneous nucleation of homogeneous particles and followed by heterogeneous particles. In the next stage, secondary nucleation induces by the crystals that were formed earlier in the nucleation stage [12]. Once the primary nucleation stage has completed and the temperature of the system is kept low, the growth process of the crystal will occur rapidly in the local region that has high concentration of molecules. Table 1 lists the current methods available to investigate the physical parameters of crude oil.

A number of mechanisms have been suggested to explain the wax deposition process. Bern *et al.*, [13] suggested that the molecular to represent wax deposition on the wall of the pipeline. Molecular diffusion is a type of mass transfer process where molecules of a component move from a high to lower concentration region by random molecular motion. This molecular motion is affected by temperature, size of the particles and viscosity of the fluid.

**Table 1**  
Methods to investigate the physical parameters of crude oil

Parameter	Method
Wax deposition	Cold disk, cold finger, cold spot test
WAT or cloud point	Differential scanning calorimeter (DSC), ASTM method
Pour point	ASTM method
Flow ability	Flow loop test, viscometry, yield stress
Formation of wax	X-ray diffraction
Wax morphology	Scanning electron microscopy (SEM), cross-polarized microscopy (CPM)

The adsorption of natural oil can be classified into two elements with a focus on the asphaltene and on the wax crystals [14]. Previous work has demonstrated that the emulsion can be stabilised by adding some fine particles such as crystals of the wax and silica where they are known as picking emulsion [15,16]. The adsorption of the wax can occur very fast at the interface of the oil-water if the wax had formed co-crystals with the addition of ester or acid molecules and without the presence of a surfactant. Surfactant can, however sometimes act as inhibitors to prevent wax deposition in the crude oil and reduces the wax adsorption on the interface of crude oil. Wax adsorption becomes more stable if it is in the continuous phase of an emulsion in state oil-wax [17]. Furthermore, an increase in temperature can cause the adsorption of wax on the interface of crude oil to decrease and gradually increases the solubility of wax.

In the case of crude oil, the molecular motion for wax deposition is dependent on the temperature. When the temperature of the crude oil is below the cloud point, wax crystals will precipitate and come out from the crude oil. In offshore pipeline, the skin temperature at the wall of the pipeline is at the lowest as the wall is directly in contact with the seabed, while at the centre of the pipeline it has the highest temperature [18]. Therefore, the gradient of the radial temperature will create a concentration gradient for the wax at the centre and at the wall of the pipeline. Thus, due to the concentration gradient, mass transfer of the wax from the centre of the pipeline towards the pipe wall is facilitated by molecular diffusion [18]. Mass transfer for wax deposition can be represented by Fick's Law as (Equation 1).

$$\frac{dm_w}{dt_w} = \rho_w D_w A_d \frac{dc_w}{dr} \quad (1)$$

where  $m_w$  the mass of wax is deposited,  $\rho_w$  is the density of the solid wax,  $D_w$  is the diffusion coefficient for liquid wax in crude oil,  $A_d$  is the surface area where the deposition occurs,  $\frac{dc_w}{dr}$  is the radial concentration gradient and  $t_w$  is the time of the deposition rate.

Other than molecular diffusion, other mechanisms have been proposed to describe the wax deposition mechanism. However, some have not been accepted such as Brownian diffusion, gravity settling, and shear dispersion. This is because the proposed mechanisms do not give clear description as to how they can significantly affect on the wax deposition [18].

### 3. Remediation Methods of Wax Deposition

Several methods to control and mitigate the wax deposition have been practised by oil production companies. The strategies for the removal of wax deposition that have been implemented are based on one or a combination of the following methods:

- I. Pipeline pigging
- II. Thermal insulation and pipeline heating

### III. Chemical (solvent) treatment

#### 3.1 Pipeline Pigging

The term “pig” in oil and gas industry refers to a type of device that is exclusively used to clean the crude oil pipeline. Pigging has been the most common method to employ when the wax has formed on the wall inside the pipelines. Through scouring action of the device, the wax deposited inside the pipeline will be scraped and removed regularly. To ease the pigging operation, a system that has dual-flowline design that allows pigging must be constructed. When the wax deposit develops excessively thick, there will be inadequate pressure to push the pig through the line as the wax accumulates in front of it. Nevertheless, there is a drawback for this method. Pigging will require the system to be shut down for 1 to 3 operating days and this will incur loss of revenue. The cost in itself to perform pigging is, however costly [19].

#### 3.2 Thermal Insulation and Pipeline Heating

It is well known that wax will start to crystallize when the temperature of the crude is below its cloud point or the wax appearance temperature. Thus, having a good thermal insulator along the pipeline is important as the insulation can maintain the temperature of the system above its cloud point. Deposition of wax will occur in the storage tank when the temperature of the tank drops below the cloud point of the crude oil.

To overcome this problem, hot fluid or electric heating is used to remove wax for short flowlines and downhole. The wax will be heated at temperature above its cloud point by hot water or oil, or steam that is flowed inside the system. The wax is then removed from the wellbore so that it will not redeposited again in the system.

#### 3.3 Chemical (Solvent) Treatment

Compared to the above methods, solvent treatment is often the most successful to remove wax deposition, and yet it has the highest cost. Therefore, this method is only carried out when the thermal method shows little success. Solvent treatment method works by using a suitable chemical that has the solvent to dissolve the wax deposited on the wall of the pipeline until the solvent is saturated and its capacity to dissolve further wax is stopped [18].

Nimer *et al.*, [20] used toluene and methyl ethyl ketone (MEK) as the inhibitors for solvent removal method. Toluene is used to remove the wax crystals from any oil surfaces and followed by the usage of methyl ethyl ketone (MEK) to further precipitate the wax crystals. Nimer *et al.*, [20] proposed that the ratio of the crude oil should be lower than the solvent ratio because increases in solvent quantity can solubilise the crystallised form of the wax. His earlier work shows that the ratio should be within 16:1 or 32:1 on a mass basis. The optimum operational conditions is with 75% MEK, a solvent to oil ration of 20:1 at -17°C in 30 min with retention time of 20 min. The wax that has been consists of a smaller amount of 6% of lighter n-paraffins. Tolune could be substituted with another solvent, for example butanol or benzene and MEK with Methylcyclohexane (MCH) to obtain different set of optimum operational conditions.

#### 4. Preventive Technique Using Wax Inhibitors Additives

Although pigging has been the most popular method to remove wax deposits, however, its use is minimized due to its high cost [19]. Consequently, wax inhibitor is often employed due to lower cost. Wax inhibitor can effectively lessen the rate of wax deposition which, in turn delays the build-up of wax on solid surface [6].

The effectiveness of wax inhibitors is influenced by temperature, wax concentration and shear rate of the inhibitors. In previous works, a high-pressure micro differential scanning calorimeter was used to measure the solubility curve of wax deposition under the WAT. In addition, Hosseinipour *et al.*, [21] have used carbon dioxide to control the initial nucleation of wax crystals. Wax inhibitors should be used for Malaysian crude oil and it is recommended that the Malaysian petroleum industry is not to use single pipeline due to the high value of WAT since the average the temperature of seabed is usually at 25°C and below [21].

Wax inhibitor that exhibit characteristics as wax crystal modifiers are chemical compound that has the same chemical structure as the wax in the crude oil. Typical compounds selected as the modifiers are usually polymeric compounds consist of one or more hydrocarbon chain molecules that are similar to the wax, but with a polar portion. This type of materials will agglomerate with the wax by bonding the hydrocarbon chains of wax molecules on the crystal lattices. In addition, the inhibitor will hinder the wax crystal growth, which in turn lower the cloud point of the crude oil [22]. Hoffmann and Amundsen [23] found that the thickness of the wax could be reduced by 60% to 90% depending on the concentrations. Theyab *et al.*, [24] have used polymers that are classified as pour points depressants to solubilize the wax crystals in pipelines.

Previous works on flow improvers that act as pour point depressants, such as maleic anhydride and n-alkyl oleate, have demonstrated that the crude oil transportation along the pipelines could be significantly improved [5]. The free radical polymerisation was measured with the Fourier transform infrared spectroscopy (FTR) and the gel permeation chromatography (GPC). The results showed that the apparent viscosity, plastic viscosity and the yield value were all reduced to the appropriate values.

The behaviour of the crude oil has also been investigated in term of its rheological properties with or without the inhibitors acting as pour point depressants (PPD). The polymer that has been used is that ethylene vinyl acetate (EVA) polymer with Iranian waxy crude oil. The polymers selected based on the content of nitrogen, carbon, hydrogen, and the molecular weight of the polymer [4]. The results indicated that the viscosity is dependent on the shear rate and the temperature of the inhibitors. The formation of the gel network increased the viscosity of the crude oil when the temperature of the wax was reduced in between 5°C and 30°C.

These wax inhibitors chemically modify the structure of the wax crystals and therefore reduce their growth in the pipeline. Previous studies have demonstrated that these inhibitors can only reduce the growth of the paraffin waxes but do not terminate the deposition process of wax which may lead to a continuous deposition in the pipelines [25].

Additives that act as pour point depressant may, however, be inefficient as flow improvers. Sanjay *et al.*, [9] stated that the efficiencies of pour point depressant and flow improver are dependent on following factors: (a) the solubility of additive in crude oil, (b) the number of pendant alkyl side chains and the distance between these, (c) the monomer ratio in the copolymer additive must be taken into consideration, (d) the crystalline and amorphous parts of the additive, (e) the chemical and physical stabilities of the additive. Example additives are: mono- and copolymers of ethylene vinyl acetate copolymers [22], methacrylate and polyalkyl acrylates [26] and maleic anhydride copolymers [27].

#### 4.1 Ethyl-Vinyl Acetate (EVA)

Typical materials that are usually chosen to act as crystal modifiers are polymeric compounds. Many kinds of polymers have been investigated for their effectiveness as modifiers. Ethyl-vinyl acetate (EVA) has been widely used as it has the ability to control the size of the wax crystals formed [28]. EVA is a polymer that consists of a linear chain of polyethylene fragment and vinyl acetate molecule.

Machado *et al.*, [22] have studied the effects of EVA20, EVA30, EVA40 and EVA80 on the oil viscosity and the pour point at 4°C. It was found that EVA30 and EVA40 showed a higher viscosity reduction in comparison to EVA20 and EVA80 at the optimum condition and EVA80 has the lowest efficiency. On pour point reduction property, EVA40 exhibits the higher efficiency than EVA30 as the pour point depressant for the Brazilian crude oil. Ashbaugh *et al.*, [29] have proposed that the efficiency of the additive to improve flowability decreases with the carbon number of the wax crystals. Jafari *et al.*, [30] used scanning electron microscopy (SEM) to observe the wax crystal morphology. It was observed that EVA copolymers could greatly reduce the size of wax crystals and rearrange plate-like shape to a spherical and denser morphology [30].

Anisuzzaman *et al.*, [25] have evaluated the performance of EVA with methyl methacrylate (MMA) and diethanolamine (DEA) and found that EVA co-DEA reduced the pour point of the crude oil by 5°C and the paraffin inhibition efficiency at 28.4%. However, the viscosity of the crude oil did not reduce sufficiently. Ridzuan and Al-Mahfadi [31] evaluated the rate of wax deposition for Malaysian crude oils using cold-finger, one-factor-at-a-time (OFAT) method with EVA. They obtained 63.5% efficiency of paraffin inhibition at a stirring rate at 400 rpm and the temperature at 10°C gave. Response surface methodology (RSM) approach was applied to minimize the amount of wax deposition using central composite design (CCD) and the results of the evaluation showed that the optimum condition for the target was achieved at 400 rpm and 19°C respectively for the stirring rate and the temperature. He *et al.*, [32] combined EVA with a modified montmorillonite (MMT) to create a nano-hybrid flow improver for China waxy crude oils. They showed that the hybrid pour point depressant exhibited a higher performance in reducing the viscosity by 82.1% than the 75.7% reduction with commercially developed pour point depressants. In terms of pour point, there was a reduction of 9°C at 100 ppm of depressant and the efficiency decreased as the concentration was increased beyond 100 ppm. The mechanism for the hybrid pour point depressant was not explained due to its complexity. The performance of EVA copolymer with polymethylsilsesquioxane (PMSQ) was investigated by Yang *et al.*, [33] for crude oil from Qinghai oilfield in China. They showed at 50 ppm EVA with 2.5 ppm PMSQ gave the strongest effect to improve the flow of waxy crude oil by up to 45.8% and the pour point was reduced from 31°C to 18°C. Higher concentration of PMSQ did not give any further improvement towards the flow behaviour. Nevertheless, the addition of PMSQ enhances the performance of EVA.

#### 4.2 Alkyl Acrylate Copolymer

A solid form of polymer acrylate polymer has also been used as a pour point depressant by Admiral *et al.*, [34]. They found that the use of acrylate polymer could enhance the ability of a crude oil to flow in the pipeline. Alkyl acrylate that contains various sets of alkyl group with carbon number ranging from C<sub>14</sub> to C<sub>26</sub> is one of the most extensively explored classes for paraffin depressants. Previous studies have suggested that combining alkyl acrylate with the other co-monomers could further reduce the pour point of crude oils than using only alkyl acrylate polymer [35]. It has been

proposed that the efficiency is influenced by the alkyl chain length and the polarity of the polymer [36].

The viscosity of traditional acrylate polymer is usually lower when in solid form than the emulsified form. Emulsified PPD of acrylate polymer (Trade name: PD90) can be created to form droplets of PPD and it shows greater reduction of PPD than the solvent based on depressant (Trade name: PD90). This is because the kinetic energy of emulsified PD90 is higher than the pure PD90, and thus causes the molecules of wax to move freely around the molecules of crude oil and therefore inhibits the crystallization of wax [34].

Deshmukh and Bharambe [37] synthesized five different composite of *n*-alkyl acrylates-co-*N*-hexadecylmaleimide to investigate the rheological properties of Nada crude oil. Their result showed that the crude oil viscosity was reduced from 90.8 mPa.s to 11.27 mPa.s at 27 °C with additive used. However, the reduction was minimal at 21°C. Indeed, there was an increased in viscosity for three types of the additives. However, the effectiveness of the additives was enhanced in reducing the pour point of the crude oil when the concentration and the alkyl chain were increased.

Litvinets *et al.*, [38] demonstrated the effect of polyalkyl acrylate containing ammonium on the rheological properties of two types of Siberian crude oil, coded R and W. The results showed that the viscosity of the crude oil from W and R fields was decreased by 22.4% and 87.7% respectively. They suggested that the optimum additive concentration at 0.05%. However, the additive showed little impact on pour point reduction for crude oil from W field and a small reduction of 7.5°C for crude oil from R field.

Yao *et al.*, [39] utilized organic nano-clay particles with polyoctadecylacrylate to serve as pour point depressant for Changqing waxy crude oil. The nanocomposite provided sites for wax nucleation where wax particles accumulated and precipitated. The pour point of the waxy crude oil was reduced by 9°C at 800 mg polyoctadecylacrylate per kg of clay. At this level, the raw waxy crude oil viscosity was decreased by 33.8%. Earlier work of Yang *et al.*, [40] was used differential scanning calorimetry (DSC) to show the morphology of the wax crystals changed into compact spherical template that suppressed the gelation point.

Chen *et al.*, [41] used the castoffs from polymethyl and methacrylate to synthesise polymethacrylate for use as an additive in crude oil. They found that a pour point reduction of 7.1°C could be achieved with a viscosity reduction of 64.5% from the original viscosity. The results from the differential scanning calorimetry showed that polymethacrylate affected the crystallization of wax in crude oil, and thus inhibited the wax crystallization.

### 4.3 Maleic Anhydrides Copolymer

Al-Sabagh *et al.*, [42] investigated the rheological properties of Quran waxy crude oil using styrene-maleic anhydride (SMA) copolymer esters to improve the flow. Four types of SMA, labelled as PPD1, PPD2, PPD3 and PPD4, were prepared with different fatty alcohols through the esterification process. It was found that PPD4, the longest chain of fatty acid decreased the viscosity of the Quran crude oil from 110 mPa.s to 24 mPa.s. This was due to the increased in the solubility of paraffin wax with increasing in length of the alkyl chain. This was in agreement with Xu *et al.*, [43].

Soliman *et al.*, [44] studied the synthesis and the performance of maleic anhydride copolymers with alkyl linoleate or tetra-esters as flow improvers and pour point depressants on Egyptian (Alamin) waxy crude oil. Two samples of flow improver were prepared and coded as PALCOSA and PALCOTE. These synthesized flow improvers were reduced the pour point from 24°C to 6°C and 3°C respectively. Similarly, the viscosity was reduced from 376.56 mPa.s to 86.51 mPa.s and 83.50 mPa.s respectively. They discovered that the efficiency of these co-polymers was affected through their link

with the asphaltenes and the paraffins which could reduce the van der Waals interaction between the molecules. The weaker interaction would eventually loss control to the energy needed to overcome the cohesiveness and adhesiveness between the oil components.

El-Ghazawy *et al.*, [45] evaluated a flow improver using a modified maleic anhydride-co-octadene towards the Norpetco Egyptian crude oil. Three types of samples were prepared through the esterification. At 9°C, the viscosity of the crude oil was decreased from 2940 mPa.s to 65.2 mPa.s when treated with the flow improver. The efficiency of the synthesized flow improver was affected by the carbon number in the chain, equilibrium of the hydrophobic molecule and the polar groups from the additive, the molecular weight and composition of the copolymer, ability to crystallize and the melting temperature of the additive.

Wu *et al.*, [46] evaluated a modified maleic anhydride and found that a greater reduction could be achieved with polymer containing aromatic rings which reduced the pour point by 19°C and a 88.4% reduction in viscosity at 26°C. Xu *et al.*, [43] evaluated the effect of maleic anhydride copolymer with phenyl (AMAC), octadecyl (MAC) and naphthalene (NMAC). The copolymers were ranked as AMAC > MAC > NMAC for their flowability.

#### 4.4 Other Type of Additive

Other types of additives have been developed and tested. Chen *et al.*, [47] tested the crude oil from China oilfield with cyclohexanone pentaerythritol ketal as the flow improver and PPD. The additive was found to be suitable as flow improver which significantly reduced the flow of the crude oil by 70%, the highest among all the additives tested. However, it was not suitable as a PPD since the pour point was only slightly decreased.

A newer type of polymer, known as terpolymer, created by combining different types of polymers to produce a varieties of multicomponent polymers by varying the concentrations of the monomers. Incorporation of the hydrophobic part in the polymer could be effective in enhancing the viscosity reduction due to the intermolecular association [48]. Comb-shaped copolymers were synthesized to obtain poly(hexyl oleate-co-hexadecyl maleimide-co-*n*-alkyl oleate). The poly(hexyl oleate-co-hexadecyl maleimide-co-*n*-alkyl oleate) was employed to investigate its effect towards Langhnaj crude oil [5]. The additives decreased the pour point by 6 °C and reduced the viscosity by 67.7%. Castro *et al.*, [49] have identified the key parameters to control the efficiency of the additive were the molecular weight and the composition of the monomers in the terpolymer.

Another copolymer was synthesized by amination of terpolymer containing monomers of octadecyl acrylate, vinyl acetate and maleic anhydride [50]. This type of additive depressed the Shengli crude oil pour point by 11°C. It was also observed that the formation of the nucleators of the wax crystals was influenced by the presence of resin, asphaltene and additive which could enhance the flowability of the crude oil. Further work by Shang *et al.*, [51] used octadecyl methacrylate, maleic anhydride and styrene monomers initiated by benzoyl peroxide. This type of paraffin inhibitor could reduced the rate of wax deposition by 50% at a molar ratio of 9:1:1. Chen *et al.*, [52] produced polyaminoamide (PAA) through aminolysis and poly-condensation of vegetable oil. They showed that PAA polymers were effective to inhibit wax deposition and those synthesized from canola oil and polyethylene polyamine gave the highest inhibition efficiency of 66.2%. Elbanna *et al.*, [53] used octadecene copolymerized with styrene to obtain  $\alpha$ -olefin styrene copolymers through a series of reaction of alkylation, esterification and amidation processes. This type of copolymer was capable to depress the pour point of crude oil by to 6°C and to inhibit the paraffin deposition by 80%. They concluded that the best additive for crude oil was when the molecular weight of the copolymer was the highest. It was also found that the addition of octadecene styrene ester and amide could

enhance the thermal stability and the performance of the additive. This phenomenon occurs due to the nitrogen group polarity which increases the electronegativity of the copolymer produced. Table 2 summarizes the efficiency of the various polymeric additives.

**Table 2**  
Efficiency of the various polymeric additives

Additive	Cond.	Sample oil	Pour point reduction (°C)	Viscosity reduction (%)	Ref.
EVA	500 ppm, 4°C	Albacora 2, Brazil	>26 >26 >26	N/A N/A N/A	[22]
EVA-co-diethanolamine	1 g EVA + 5 mL DEA, 4°C	Malaysian crude oil	5	7.53	[25]
EVA with modified montmorillonite	100 ppm, 30°C	Jinqiao Pipeline Company, Xuzhao, China	9	82.1	[32]
EVA copolymer with polymethylsilsequioxane	50 ppm EVA + 2.5 ppm PMSQ, 24°C	Qinghai waxy crude oil	18	45.78	[33]
<i>n</i> -alkyl acrylates-co- <i>N</i> -hexadecylmaleimide	1000 ppm, 24°C	Nada crude oil, Gujerat, India	27	87.88	[37]
Polyalkyl acrylate contained ammonium	0.1 wt%, 15°C	Verkhne-Salatskoye	1.6	22.39	[38]
Polyoctadecylacrylate	0.05 wt%, 15°C	Urmanskoye	7.5	87.69	
	800 mg/kg POA/clay, 5°C	Changqing, China	9	33.75	[39]
Polymethacrylate	500 ppm, 50°C	Jinghe, China	5.4 3.2	49.9 30.7	[41]
Polystyrene-maleic anhydride	10000 ppm, 27°C	N/A	30	78.18	[42]
Maleic anhydride copolymers with alkyl linoleate or tetra-esters	5000 ppm, 15°C	Alamin, Egypt	18	77.03	[43]
	3000 ppm, 15°C		18	77.34	
Maleic anhydride-co-octadene	3000 ppm, 9°C	Norpetco, Egypt	24 18	97.78 96.05	[44]
Modified maleic anhydride copolymer	500 ppm, 26°C	Changqing crude oil	9 12 13 19	N/A N/A N/A 88.4	[45]
Cyclohexanone pentaerythritol ketal	500-1000 mg/L, 20°C	Jinghe, China Xinjiang, China	2.7 2.4	58.06 42.05	[46]
Poly(hexyl oleate-co-hexadecyl maleimide-co- <i>n</i> -alkyl oleate)	1000 ppm, 16°C	Langhnaj, India	3 6 6	54.55 67.68 56.23	[5]
$\alpha$ -olefin styrene	2000 ppm, 60°C	Western Desert, Egypt	21	N/A	[52]

## 5. Conclusions and Recommendations

We have reviewed the various techniques and the recent advances of the polymeric additives that have dual functions as flow improver and as pour point depressant in crude oil. Based on the discussions, the following conclusions can be drawn:

1. The efficiency of an additive is dependent on its ability to co-crystallize with the wax.

2. Additives that are usually formed by combining two or more monomers could achieve a higher reduction in viscosity and pour point of the crude oil than the monomer themselves.
3. A wide range of polymeric crystal modifiers have been evaluated to assess their effectiveness towards different types of crude oils. Nevertheless, there is a major need in theoretical modeling to correlate the relationship between the various types of polymers to enable prediction of their efficiency to inhibit wax in the future. Furthermore, studies involved in using different solvent together with crystal modifier are needed to identify the best combination of solvent and polymers for the different type of crude oils.

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### References

- [1] Leckel, D. "Diesel production from Fischer–Tropsch: the past, the present, and new concepts." *Energy & Fuels* 23, no. 5 (2009): 2342-2358.
- [2] Ahmed, T.H. *Equations of state and PVT analysis : applications for improved reservoir modeling* (2nd ed.). Gulf Professional Publishing, Houston, Texas. (2007): 457-505.
- [3] Frigaard, I., Vinay, G., and Wachs, A. "Compressible displacement of waxy crude oils in long pipeline startup flows." *Journal of Non-Newtonian Fluid Mechanics* 147 no. 1-2 (2007): 45-64.
- [4] Behbahani, T.J., Akbar, A., Beigi, M., Taheri, Z., and Ghanbari, B. "Investigation of wax precipitation in crude oil : Experimental and modeling." *Petroleum* 1, no. 3 (2015): 223-230.
- [5] Patel, M. R., Chitte, P. S., and Bharambe, D.P. "Oleic acid based polymeric flow improvers for Langhnaj (North Gujarat, India) crude oil." *Egyptian Journal of Petroleum* 26, no. 4 (2017): 895-903.
- [6] Pedersen, K.S., and Ronningsen, H.P. "Influence of wax inhibitors on wax appearance temperature, pour point, and viscosity of waxy crude oils." *Energy & Fuels* 17, no. 2 (2003): 321-328.
- [7] Azevedo, L.F.A., and Teixeira, A.M. "A critical review of the modeling of wax deposition mechanisms." *Petroleum Science and Technology* 21, no. 3-4 (2003): 393-408.
- [8] Ganeeva, Y.M., Yusupova, T.N., and Romanov, G.V. "Waxes in asphaltenes of crude oils and wax deposits." *Petroleum Science* 13, no. 4 (2016): 737-745.
- [9] Sanjay, M., Simanta, B., and Kulwant, S. "Paraffin problems in crude oil production and transportation: a review." *SPE Production & Facilities* 10, no. 1 (1995): 50-54.
- [10] Dobbs, James B. "A unique method of paraffin control in production operations." In *SPE Rocky Mountain Regional Meeting*. Society of Petroleum Engineers, 1999.
- [11] Myerson, Allan. *Handbook of industrial crystallization*. Butterworth-Heinemann, 2002.
- [12] Ozawa, T. "Kinetics of non-isothermal crystallization." *Polymer* 12, no. 3 (1971): 150-158.
- [13] Bern, Peter A., Vincent R. Withers, and Roger JR Cairns. "Wax deposition in crude oil pipelines." In *European offshore technology conference and exhibition*. Society of Petroleum Engineers, 1980.
- [14] Emiliano A.L., Daniel-Ricardo M.V. and Arlex C.G. "Review of studies on asphaltene – wax interaction and the effect thereof on crystallization." *Journal of oil, gas and alternative energy sources* 5, no. 5 (2014): 39-53.
- [15] Binks B.P., "Particles as surfactants—similarities and differences." *Current Opinion in Colloid & Interface Science* 7, no. 1-2 (2002): 21-41.
- [16] Tyowua A.T. Yiase S.G.-Binks B.P. "Double oil-in-oil-in-oil emulsions stabilised solely by particles." *Journal of Colloid and Interface Science* 488, (2017): 127-134.
- [17] Ma, Q., Wang, W., Liu, Y., Yang, J., Shi, B., and Gong, J. "Wax adsorption at paraffin oil–water interface stabilized by Span80." *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 518, (2017): 73-79.
- [18] Guo, B., Song, S., Ghalambor, A., Lin, T.R., *Offshore pipelines: Design, installation and maintenance*. USA- Gulf Professional Publishing, 2014.
- [19] Wei, B. "Recent advances on mitigating wax problem using polymeric wax crystal modifier." *Journal of Petroleum Exploration and Production Technology* 5, no. 4 (2015): 391-401.
- [20] Nimer, Amel A., Abdelshakour A. Mohamed, and Ali A. Rabah. "Nile Blend Crude Oil: Wax Separation Using Mek Toluene Mixtures." *Arabian Journal for Science and Engineering* 35, no. 2 (2010): 17.
- [21] Hosseinipour A, Azuraian J.J, and Yusup S. "The effect of CO<sub>2</sub> on wax appearance temperature of crude oils." *Procedia engineering* 148, (2016): 1022-1029.

- [22] Machado, A.L.C, Lucas, E.F., and González, G. "Poly(ethylene-co-vinyl acetate) (EVA) as wax inhibitor of a Brazilian crude oil: oil viscosity, pour point and phase behavior of organic solutions." *Journal of Petroleum Science and Engineering* 32, no. 2-4 (2001): 159-165.
- [23] Hoffman, R. and Amundsen, L. "Single-phase wax deposition experiments." *Energy & Fuels* 24, (2010): 1069-1080.
- [24] Theyab, M.A., and Diaz, P. "Experimental Study on the effect of inhibitors on wax deposition." *Journal of Petroleum & Environmental Biotechnology* 7, no. 6 (2016): 1-5.
- [25] Anisuzzaman, S.M., Abang, S., Bono, A., Krishnaiah, D., Karali, R., and Safuan, M.K. "Wax inhibitor based on ethylene vinyl acetate with methyl methacrylate and diethanolamine for crude oil pipeline." *IOP Conference Series: Materials Science and Engineering* 206, no. 012074 (2017): 1-8.
- [26] Kok M.V.\_ "The effect of pour point depressant on the flow behavior of crude oils." *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects* 36 no. 2 (2014): 167-172.
- [27] Son, A.J., Graugnard, R.B., and Chai, B.J. "The effect of structure on performance of maleic anhydride copolymers as flow improvers of paraffinic crude oil." *In SPE International Symposium on Oilfield Chemistry*. Society of Petroleum Engineers. (1993).
- [28] Vieira, L.C., Buchuid, M.B., and Lucas, E. F. "Effect of pressure on the performance of poly(ethylene-vinyl acetate) as wax deposition inhibitors by calorimetric method." *Journal of Applied Polymer Science* 126, no. 1 (2012): 143-149.
- [29] Ashbaugh, H.S., Guo, X., Schwahn, D., Prud'homme, R.K., Richter, D., and Fetters, L.J. "Interaction of paraffin wax gels with ethylene/vinyl acetate co-polymers." *Energy & Fuels* 19, no. 1 (2005): 138-144.
- [30] Jafari Ansaroudi, H.R., Vafaie-Sefti, M., Masoudi, S., Behbahani, T.J., and Jafari, H. "Study of the morphology of wax crystals in the presence of ethylene-co-vinyl acetate copolymer." *Petroleum Science and Technology* 31 no. 6 (2013): 643-651.
- [31] Ridzuan, N., and Al-Mahfadi, M. "Evaluation on the effects of wax inhibitor and optimization of operating parameters for wax deposition in Malaysian crude oil." *Petroleum Science and Technology* 35, no. 20 (2017): 1945-1950.
- [32] He, C., Ding, Y., Chen, J., Wang, F., Gao, C., Zhang, S., and Yang, M. "Influence of the nano-hybrid pour point depressant on flow properties of waxy crude oil." *Fuel* 167, (2016): 40-48.
- [33] Yang, F., Yao, B., Li, C., Shi, X., Sun, G., and Ma, X. "Performance improvement of the ethylene-vinyl acetate copolymer (EVA) pour point depressant by small dosages of the polymethylsilsequioxane (PMSQ) microsphere: An experimental study." *Fuel* 207, (2017): 204-213.
- [34] Admiral, A., Abdullah, M. K., and Ariffin, A. "Evaluation of emulsified acrylate polymer and its pour point depressant performance." *Procedia Chemistry* 19, (2016): 319-326.
- [35] Kazantsev, O.A., Volkova, G.I., Prozorova, I.V., Litvinets, I.V., Orekhov, D.V., Samodurova, S.I., Kamorin D.M., Moikin A.A., and Medzhibovskii, A.S. "Poly(alkyl (meth)acrylate) depressants for paraffin oils." *Petroleum Chemistry* 56, no. 1 (2016): 68-72.
- [36] Erceg Kuzmić, A., Radošević, M., Bogdanić, G., Srića, V., and Vuković, R. "Studies on the influence of long chain acrylic esters polymers with polar monomers as crude oil flow improver additives." *Fuel* 87, no. 13-14 (2008): 2943-2950.
- [37] Deshmukh, S., and Bharambe, D.P. "Synthesis of polymeric pour point depressants for Nada crude oil (Gujarat, India) and its impact on oil rheology." *Fuel Processing Technology* 89, no. 3 (2008): 227-233.
- [38] Litvinets, I.V., Prozorova, I.V., Yudina, N.V., Kazantsev, O.A., and Sivokhin, A.P. "Effect of ammonium-containing polyalkyl acrylate on the rheological properties of crude oils with different ratio of resins and waxes." *Journal of Petroleum Science and Engineering* 146, (2016): 96-102.
- [39] Yao, B., Li, C., Yang, F., Sjöblom, J., Zhang, Y., Norrman, J., and Xiao, Z. "Organically modified nano-clay facilitates pour point depressing activity of polyoctadecylacrylate." *Fuel* 166, (2016): 96-105.
- [40] Yang, F., Paso, K., Norrman, J., Li, C., Oschmann, H., and Sjöblom, J. "Hydrophilic nanoparticles facilitate wax inhibition." *Energy & Fuels* 29, no. 3 (2015): 1368-1374.
- [41] Chen, G., Yuan, W., Zhang, F., Gu, X., Du, W., Zhang, J., Li J., and Qu, C. "Application of polymethacrylate from waste organic glass as a pour point depressor in heavy crude oil." *Journal of Petroleum Science and Engineering* 165, (2017): 1049-1053.
- [42] Al-Sabagh, A.M., Noor El-Din, M.R., Morsi, R. E., and Elsabee, M.Z. "Styrene-maleic anhydride copolymer esters as flow improvers of waxy crude oil." *Journal of Petroleum Science and Engineering* 65, no. 3-4 (2009): 139-146.
- [43] Xu, J., Zhang, X., Sun, J., Li, L., and Guo, X. "How comb-type poly(maleic acid alkylamide-co- $\alpha$ -olefin) assemble in waxy oils and improve flowing ability." *Asia-Pacific Journal of Chemical Engineering* 4, no. 5 (2009): 551-556.
- [44] Soliman, E.A., Elkatory, M.R., Hashem, A.I., and 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, (2018): 535-547.

- [45] El-Ghazawy, R.A., Atta, A M., and Kabel, K.I. "Modified maleic anhydride-co-octadecene copolymers as flow improver for waxy Egyptian crude oil." *Journal of Petroleum Science and Engineering* 122, (2014): 411-419.
- [46] Wu, Y., Ni, G., Yang, F., Li, C., and Dong, G. "Modified maleic anhydride co-polymers as pour-point depressants and their effects on waxy crude oil rheology." *Energy & Fuels* 26, no. 2 (2012): 995-1001.
- [47] Chen, G., Li, Y., Zhao, W., Qu, K., Ning, Y., and Zhang, J. "Investigation of cyclohexanone pentaerythritol ketal as a clean flow improver for crude oil." *Fuel Processing Technology* 133, (2015): 64-68.
- [48] El-Ghazawy, R.A., and Farag, R.K. "Synthesis and characterization of novel pour point depressants based on maleic anhydride-alkyl acrylates terpolymers." *Journal of Applied Polymer Science* 115, no. 1 (2010): 72-78.
- [49] Castro, L.V., Flores, E.A., and Vazquez, F. "Terpolymers as flow improvers for Mexican crude oils." *Energy & Fuels* 25, no. 2 (2011): 539-544.
- [50] Fang, L., Zhang, X., Ma, J., and Zhang, B. "Investigation into a pour point depressant for Shengli crude oil." *Industrial & Engineering Chemistry Research* 51, no. 36 (2012): 11605–11612.
- [51] Shang, H.Y., Ying, X.H., Huang, C.F., Duan, B.H., Fan, G., Liu, P.C., and Liu, C.G. "Paraffin inhibitor development and performance evaluation in Xinjiang oilfield." *Journal of China University of Petroleum* 37, (2013): 167-172.
- [52] Chen, G., Tang, Y., and Zhang, J. "Synthesis and application of polyaminoamide as new paraffin inhibitor from vegetable oil." *Chemistry Central Journal* 5, (2011): 82-84.
- [53] Elbanna, S. A., Abd El Rhman, A.M.M., Al-Hussaini, A.S., and Khalil, S.A. "Synthesis and characterization of polymeric additives based on  $\alpha$ -Olefin as pour point depressant for Egyptian waxy crude oil." *Petroleum Science and Technology* 35, no. 10 (2017): 1047-1054.