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The Progress and Evaluation of Polymeric Wax Inhibitors for Waxy Crude Oil: A-Mini Review

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Abstract

One of the main problems faced in the petroleum industry is the deposition or crystallization of wax paraffin from crude oils, especially when the temperature of the crude oil is below the wax appearance temperature. In order to increase the fluidity and wax, the oil process constantly precipitates, resulting in a series of negative pipeline output negatives and even causing full blockage under extreme conditions. Reduce waxy oil viscosity; In order to increase the fluidity and wax, the oil process constantly precipitates, resulting in a series of negative pipeline output negatives and even causing full blockage under extreme the cost of transportation of waxy crude oil pipelines is thus reduced. A brief description was made of the production of the pour point depressant and the future outlook. The groups of crystalline-amorphous copolymers, ethylene copolymers, comb polymers and nanohybrids include most polymeric additives. This paper summarizes the types of novel nano-pour point depressants, mechanisms of action and assessment tests of waxy crude oil cold flow properties and analytical methods*.*

Keywords: *Polymeric additive; Pour point depressant; Waxy crude oil; Mechanisms; Cold flow properties; Evaluation test.*

1. Introduction

Waxy crude oils are encountered throughout the world and have been produced for several decades in areas such as China, India, Egypt, and the North Sea [1–4]. These fluids contain substantial amounts of petroleum wax (usually5persnt by weight), which complicates crude oil recovery, processing, and transportation.

1.1. The Types of Wax Crystals

The key explanation for the poor fluidity of waxy crude oil is the creation of net-like or cage-like structures caused by wax precipitation. Macro-crystalline waxes and microcrystalline waxes are typically classified into petroleum waxes [5-7]. IN general, macro-crystalline waxes of mainly low molecular weight n- alkanes (C16-C40), macro-crystalline waxes precipitate at low temperature to form needle-like or platelet-like crystals [8]. Micro-crystalline waxes are composed of high molecular weight iso-alkanes and cycloalkanes [9]. The potential to mix micro-crystalline waxes with far more oil than macro-crystalline ones. Micro-crystalline waxes precipitate to form small crystals and some amorphous particles without a separate crystallization regime due to a large number of isomer permutations [10], the temperature of crude oil falls to the wax appearance temperature (WAT). In the oil process, the wax crystals begin to continuously precipitate, overlap and interlock to create a three-dimensional network structure. The state of crude oil transforms from sol to gel due to the change in external conditions [11]. When the inner wall temperature drops below the WAT, in pipeline transport, the wax is successively collected, which in turn allows the pipeline diameter to decrease and even blocks the pipeline. In order to reduce the difficulties of crude oil refining and transport and to reduce the unnecessary use of energy The addition of crude oil polymeric pour point depressants

(PPDs) or flow improvers (FIs) has been shown to be an efficient means of inhibiting wax precipitation and enhancing the low temperature flowability of crude oil [12].

Polymeric wax inhibitors (WIs) [2] are commonly applied to mitigate wax deposition in the pipeline transport of waxy crude oils. For waxy crude oils, most of the inhibitors can also be used as (PPDs) or (FIs), significantly improving protection and economy.

2. Mechanism of polymeric pour point depressants

2.1. Crystallization process of waxy crude oils

Crystallization is a physical process in which, from a disordered phase, such a strong ordinate structure is formed. Crystallization of crude oil paraffin waxes may be divided into three stages: nucleation, growth, and agglomeration [13-14].Wax molecules from the solution bulk are transferred towards the nuclei during the growth process, driving an increase in crystallite size. Developed wax crystals interlock during the agglomeration process, causing network formation. In the first point, nuclei appear in the oil process because of the super saturation of paraffin waxes. Wax molecules from the solution bulk are transferred towards the nuclei during the growth process, driving an increase in crystallite size. Developed wax crystals interlock during the agglomeration process, causing network formation.

2.2. Interactions between polymeric additives and paraffin waxes

Combination of interactions between polymeric WIs and PPDs and waxes that involve nucleation, adsorption, co-crystallization, and solubilization are important, according to [15-16].

Nucleation

Some polymeric PPDs self-assemble into micelle-like aggregates at temperatures well above the WAT that exhibit a crystalline core and soluble hairy brushes surrounding the core [17-19].

Adsorption and co-crystallization

Adsorption and co-crystallization [20-21]. At temperatures near or below the WAT, several polymeric PPDs co-crystallize with wax molecules or adsorb on growing surfaces of precipitated wax crystals [22-23]. The incorporation of polymeric WIs and PPDs into wax crystals interferes with growth, inhibits wax deposition, and improving flowability. To investigate the effects of polymeric PPDs on the growth of wax crystals, molecular dynamic (MD) simulation has been used. From side view of the morphology of paraffin crystal [24] displays the lateral view of the morphology of an idealized paraffin wax crystal with the assistance of MD [24]. On (001) facets, chain addition procedures proceed faster than on other facets, producing plate-like crystals. The nonpolar groups can integrate into the lattice of wax crystal cells when polymeric WIs and PPDs are present, while the polar groups extend beyond the (001) facet. The morphology can then shift from plate-like to a structure with more integrity [24] (such as spherulitic-like).

Solubilization

With the more concentration of PPD in crude oil, instead of crystals with long- stick- like- or plate-like structures, more and more thin, spherulitic- like crystals appear. The solid particles act as a dispersion process while the liquid acts in the crude oil method with precipitated wax crystals as a continuous phase [25]. In the absence of PPDs that are polymeric, there is a broad solid-liquid interface between the wax crystal and the liquid phase in the absence of polymeric PPDs, and the system's energy is very high, leading to system instability. The solid-liquid interface must be reduced in order to decrease the system's energy, but it would lead to wax crystal coalescence [26]. Therefore, wax crystals appear to form large solid crystals and then create a three-dimensional structure of the network. The high dispersion of small wax crystals can be assured by the addition of polymeric PPDs [27]. The polar groups are produced on the surface of the eutectic by polymeric additive molecules and wax crystal. Substances with low molecular polarity in crude oil are preferentially absorbed to form the first molecular layer by the polar groups on the eutectic surface. The secondary layer, also referred to as the solvation layer, is caused by the first layer adjacent to it; it resides on the eutectic outer surface. The presence of the solvation layer alters the essence of the wax crystal-liquid interface, resulting in a decrease in the system's surface energy. The solvation layer prevents the wax crystals from binding, which does not lead to the creation of a three-dimensional network structure [28-29].

3. Types of polymeric pour point depressant

There are various mechanisms by which chemical inhibitors in pipelines can prevent wax deposition or gelling. In order to prevent their agglomeration and deposition, they may lower the WAT or pour point, or adjust the wax crystals. The WAT altering chemicals are typically referred to as wax inhibitors or modifiers of wax crystals, Although those affecting the pour point are referred to as (PPDs) or (FIs); Although there is a great deal of overlap in terms of the chemistry and mechanisms of these two groups, certain detergents or dispersants acting as WIs, such as polyesters and amine ethoxylates, can act in part to prevent adhesion by changing the pipe wall surface rather than just the wax crystals [30], And many active wax inhibitors produce weaker deposits that are easier to extract by shear forces [31]. Ethylene polymers and copolymers, comb polymers and various other branched polymers with long alkyl groups, such as alkyl phenol-formaldehyde, are the key forms of (WIs) and PPDs, which are not as efficient as comb polymers when operating on their own as flow improvers .

3.1. Ethylene copolymers

This group consists of ethylene / small alkene copolymers, copolymers of ethylene / vinyl acetate (EVA) and copolymers of ethylene / acrylonitrile [2]. More specifically, poly (ethylene-propylene) and poly (ethylene -butene) polymers are examples of such polymers used in wax inhibition studies [32]. Random, low molecular weight EVA copolymers are commonly used and investigated as WIs. The efficacy of the EVA copolymer as an inhibitor is significantly affected by the copolymer's percentage of vinyl acetate. The vinyl acetate material, which is more polar, encourages solubility and decreases crystallinity and is therefore important for WAT depression, while the polyethylene content is necessary for co-crystallization with structurally similar wax, but has little influence on crystallization on its own.

3.2. Comb polymers

Characteristic structure of a comb polymer PPD have been extensively studied by researchers such as [33-35] as wax inhibitors. They are usually made of (meth) acrylic acid or monomers of maleic anhydride, or both, which generally have a stronger wax inhibition compared to ethylene copolymers [2].Comb polymers decrease the ability of wax crystals by adding defects or repulsive forces to agglomerate into a gel structure. Comb polymers can be accomplished by providing nucleating sites on their paraffin-like pendant chains for wax crystals, while a polar backbone impedes the creation of an interlocking wax network [35]. The interaction mechanism between polymers and paraffin/asphaltene is shown by co-crystallization between nonpolar alkyl branches and long-chain paraffins, the paraffin crystals are anchored [36-37].

In the decentralized state, the polar groups surrounding the asphaltene can efficiently disperse the asphaltene and prevent the formation of the network structure. The interaction between polymers and paraffin/asphaltene can therefore effectively boost crude oil's flow ability.

3.3. Nanohybrid polymeric pour point depressants (NPPD)

While conventional polymeric PPDs are widely used in waxy crude pipeline transport, several limitations apply: (a) restricted efficacy of pour point depression on high waxy crude oils; (b) efficacy may depend on crude composition, thermal and shear history; (c) efficacy may be reduced by competitive adsorption in conjunction with heavy polar colloidal components.(e) the static long-term stability of treated crudes, due to sequestration or depletion processes, may not satisfy transport requirements. Due to specific size, high surface, and quantum tunneling effects, nanoparticles exhibit potential applications in polymer modification. Analysis was conducted [38].

The preparation of polymeric nano composites by dispersion into the polymer phase of nanoparticles. Because of the introduction of dispersed nanoparticles, nano composite properties such as mechanical and thermal stability, abrasion resistance, and tenacity are significantly improved compared with pure polymers. Recently, the [39-40]. Nanohybrid PPDs based on typical polymeric PPDs and nanoparticles have been prepared. It was found that with nanohybrid PPDs, viscosity, powder point reduction, shear resistance, and crude flowability are much better than with conventional EVA. From mechanism of nano polymer PPD for improving the flowability of waxy crude oil [37], further work is needed to explain the nanohybrid PPD process and to prepare new nanohybrid PPDs with optimum efficacy.

4. Effect of paraffinic wax with polymeric additive on viscosity

Viscosity effects can be assumed to originate from many different mechanisms, and polymeric and pending group chain lengths are two significant factors included in these mechanisms. The covalently bound polymer backbone (formally bonded, via inter-electronic energy level sharing), pending group interactions arising from London induction forces over van der Waals radii also contribute to the viscosity of the bulk system, these interactions are weaker and more susceptible to heat and shear thinning, they contribute to the viscosity of the bulk system and give the system a high resistance to heat or shear thinning. The contribution of the covalent backbone to the viscosity of the bulk structures is therefore considered irreducible under normal heating and shear conditions and is given the real Newtonian viscosity nomenclature [41-48]. The name thixotropic is given to the pendent interaction viscosity effect, which indicates that this contribution of viscosity is susceptible to shear thinning. Although the interactions between London/van der Waals are small, their higher number and high crystallinity combine to produce high viscosities at lower temperatures (conditions favoring crystallization). As the concentration of these interacting species increases, the viscosity effects of the polymer backbone can be overwhelmed and become the dominant force deciding the appearance of the gross system [49].

5. Evaluation tests of cold flow properties of waxy crude oil

Wax appearance point (ASTM D-3117)

The new method will treat darker samples as a second technique for detecting the precipitation of wax. As dependence is put on visual observations, it is similar to cloud point determination. It suffers from the effects of subcooling/superheating.

Wax appearance temperature(WAT)

For crude oils, WAT or crystallization temperature (Tc) is calculated by differential scanning calorimetry for crude oils (DSC). A precise determination of the cloud point for crude oils is this temperature.

Pour point determination (ASTM D97)

The pour point displays the lowest temperature at which the crude can flow under specified conditions (very low shear rates). For both crude oils and derived products, it is used. Laboratory experiments showed that good pour-point depression did not necessarily indicate good results on the field.

Pour point reversion

During storage, some oils containing PPDs demonstrate an improvement in the pour point test. With frequent temperature variations somewhere just above the pour point of the oil, the greatest rise is observed. The point of pour can be 40°C and even more. This effect is referred to as Pour Point Reversion. In storage, but not in operation, such as residual fuel oils after prolonged storage, pour point reversion occurs ruing storage, some oils containing PPDs demonstrate an improvement in the pour point test. With frequent temperature variations somewhere just above the pour point of the oil, the greatest rise is observed. The point of pour can be 40°C and even more. This effect is referred to as pour point reversion. In storage, but not in operation, such as residual fuel oils after prolonged storage, pour point reversion occurs.

Wax deposition test (Static cold finger test)

This test is used to determine the efficacy of FIs in inhibiting paraffin deposition during the transport of waxy crude oils by pipeline. A variety of authors have identified Paraffin Deposition Equipment. Both make use of a deposition surface cooled to a temperature below the cloud point of crude oil solution temperature under controlled conditions. The preheating temperature of the crude oil should be set according to the conditions of the field.

Rheological measurements for crude oils

Waxy crude oils typically function as Newtonian fluids at any temperature above pour point about 10°C or higher, so from single viscosity calculation their flow properties above this temperature can be predicted. Since the waxy crude oils are cooled below this temperature, they become non-Newtonian and the relationship between shear rate and shear stress must be determined to explain their laminar flow, in addition, the right fluid flow scale-up technique should be applied to assess the form of non-Newtonian fluid. One of the key factors restricting the handling of waxy crude oils or residual fuel oils in pipelines is the restarting of the line after a shutdown when the oil has quietly cooled and a gel structure has been formed.

5.1. Analytical tools

For the validation of other laboratory assessment tests, certain analytical methods are currently used. These tools are quick, simple, economical and, in most cases, offer more precise results. Some examples of instruments like this are:

Photomicrographic analysis

This research method is used for the analysis of the flow characteristics in terms of wax crystal morphology alteration. In this relation, temperature-programmed crystallization photoanalysis may provide interesting details, notably on the dependence of crystal growth, crystal size and crystal shape on the flow enhancer type and concentration.

Thermomicroscopy

Analytical methods to compare morphological changes with thermal effects-observed by calorimetry scanning differentials or structural changes. Through this process, it is possible to characterize highly crystalline areas corresponding to the precipitated n-alkanes in the hydrocarbon matrix.

Differential scanning calorimetry (DSC)

By determining the crystallization temperature (Tc) at which the thermal power produced by the heat of crystallization of paraffins is 15μw, this method is used to accurately calculate the wax appearance temperature. Only on the temperature scale is the initiation of nucleation / crystallization suppressed. DSC tests the rate at which the sample absorbs or evolves energy. Heats of transition may be determined.

Infrared spectral analysis

The interactions of pour point depressants with wax, resin and asphaltene fractions of crude oils were realized by infrared spectroscopic studies by changing the orientation of the aliphatic portion of these fractions. Qualitative indications of the suitability of PPDs for improving the properties of cold flow were provided by band absorbance ratios.

Pulsed NMR spectroscopy (for determining of wax deposition)

A low resolution NMR technique is now used to calculate the crystallized wax fraction as a function of temperature. The evaluation of the pulsed NMR spectroscopy system to calculate the quantity of solid versus temperature focuses on this technique.

X-Ray diffraction

Through X-ray diffraction patterns study, the interaction of pour point depressants, particularly comb form, with paraffin content of crudes, was realized. It is a matter of matching the support of their crystallite structure [50].

6. Conclusions

The structural characters, form, basic mechanisms of polymeric WIs and PPDs, and factors influencing the efficacy of polymeric PPDs are described in this review article. Non-polar groups interacting with paraffin waxes and polar groups interrupting the growth of wax crystals are found in most polymeric PPDs. Polymeric PPDs and paraffin waxes have four fundamental interactions, which can be defined as nucleation, adsorption, co-crystallization, and solubilization. Polymeric PPDs have a major influence on the microscopic morphology of wax crystals and aggregates dependent on interactions, thus effectively inhibiting wax deposition and enhancing the rheology of crude oil. The presence of asphalt has an important influence on the morphology of polymeric PPD modified wax crystals. Polymeric PPDs, Ethylene copolymers, comb polymers and nanohybrids can be classified into crystalline-amorphous copolymers. With crystalline cores and amorphous brushes surrounding the cores, crystalline-amorphous copolymers assemble themselves into a micelle-like structure.

A key factor determining the efficacy of comb polymers is the alkyl side chain length. Due to the introduction of nanoparticles in the polymer process, nanohybrid PPDs can exhibit improved efficacy, thermal stability and shear stability. The essence of the modification of waxy crude oil is to modify the eutectic and adsorption relationship between wax molecules. In order to improve the morphology of wax crystals, the formation of a three-dimensional network structure is not easy. Study the effect of paraffinic wax on viscosity with a polymeric additive. To evaluate flow additives, various test methods are adopted, some of which are standardized while others are not yet, but already carried out by additive companies, in order to get closer to field conditions.

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