PPD studies on Western onshore crude oil

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Abstract: Chemical additives used at small concentrations have been found to effectively alter the flow properties of crude oil. These products have been used for many years in solving transportation problems in onshore and offshore operation with a high degree of success. Because of the incentive increase of fluid production, assets have been more receptive to the important physical properties which control the flow behaviour. High pour point and high viscosity crude oil deposits at the wellbore tubing, flow line and pipelines can have catastrophic consequences both in loss of oil and environmental hazards caused by pipeline ruptures. Various methods have been designed to reduce the pour pint and viscosity of high asphaltene - wax content crudes. Different products (Pour Point Depressant,PPD) were evaluated on composite oil sample collected from western onshore field.

Keywords: Flow assurance**,**Pour point, Pour point depressant. Viscosity

I. Introduction

Flow assurance involves ensuring fluid flow in well, flow line and trunk line. Transportation of crude oils with high viscosity makes it difficult to flow through the pipelines. Thus, transportation of crude oil from the wellbores to the refinery gate isimportant as their production has to be secured through flow assurance. Great amount of capital is consumed annually by the petroleum companies for the prevention and removal of wax in production and transportation oil lines. It has been established that paraffin's are mostly responsible for this problem. These solid particles deposit in production tubing, pipelines, processing equipment's and ultimately source plugging in the operations. The cost of production can be reduced from accurate prediction of Wax Appearance Temperature (WAT) and the amount of wax likely to be deposited.

Fig.1 – Blockage in Crude Oil Pipelines

During flowing of crude oil through a long pipeline, it is important to take an account of viscosity, acidity and salinity for field operations. The process of ensuring a constant flow of oil against different issues which can cause flow difficulty is known as **Flow Assurance.**.

Asphaltene

Asphalteneare the complex carbon-based molecules distinguish by groups of interconnected aromatic rings. They can cause flow problems, particularly in the well itself as well as in the refinery lines. Asphaltene solubility and precipitation needs considerable attention.

Cloud point

Cloud point is the temperature at which paraffin wax begins to crystallize.It can be identifiedby the onset of turbidity as the temperature is lowered. In other words, Cloud point is the highest temperature at which the wax crystals are formed. The cloud point of particular crude depends on the oil composition and is affected by little amounts of paraffin in the crude. Crystals of wax begin to precipitate from the oil phase when the temperature falls below the cloud point.

Pour point

Pour point is the temperature at which the liquid ceases to flow and is observed to flow when heated under prescribed conditions. Therefore, the crystal of waxes or paraffin’s start to dissolve as their temperature reaches the pour point.

The key controlling factors of Wax deposition are as follows:

- The temperature difference between fluid and pipe wall (thus the heat flux)
- The concentration gradient
- The mass transfer resistance determined by fluid properties and flow rate.

Effect of pressure on the formation of wax in a single phase system and multiphase system.

In a single-phase oil system, since the wax phase is heavy than the oil, an increase in pressure slightly increases the wax deposition tendency.

In a multiphase system, an increase in pressure causes the light ends of the mixture into the liquid phase and tends to decrease the cloud point, thereby tending to lower the amount of wax formed at a particular temperature.

Paraffin precipitation is normally related with changes in the physical environment surrounding the crude oil. Due to the normal subsurface temperature gradient, and the hydrostatic pressure variation in crude oil, when the oil is produced up the tubing, a pressure and temperature change occurs. This allows the lighter hydrocarbons to break out of solution and become a gas phase. These lighter hydrocarbons help keep the heavy end paraffin in solution. Precipitation may also take place due to sudden pressure drops.

II. Material and Methods

Methods of Flow Assurance Control:

Generally, there are three basic methods of conductinghydrates, waxes, and asphaltene: thermal, chemical, and mechanical. They may be used alone or in combination.

Thermal methods surround heat conservation using a submissive insulation system, an active addition of heat, or an active system of insulation and heating. The active heating can be fluid heating, electric heating, or thermal-chemical exothermal heating.

Chemical methods cover both inhibition and dehydration for hydrate prevention and the use of long chain polymers to continue waxes and asphaltene in the fluid.

Mechanical methods means, such as pigs, may be used for "prevention" if operated on a planned frequency. Another mechanical tool is coiled tubing. Pigging is the oldest way of cleaning out a flow line - by mechanically scraping the inside of the line. Pipeline pigs travel the length of a pipeline operated by fluid. A variety of pigs, either soluble (gel pigs) or insoluble, are introduced into the flow line.

There are three ways currently in use to combat the formation of hydrates:

- Preservation and application of heat by using insulation and supplemental heating
- Use of inhibitors

Removal of sufficient water from the stream so that formation of hydrate does not take place.

Prohibition of the hydrate formation process is a commonly used in practice. There are two kinds of inhibition - thermodynamic and kinetic. Thermodynamical inhibition prevents hydrate formation by adding a third active component into a two-component/ intermolecular interaction and thermodynamic equilibrium between molecules of water and gas, and to modify the hydrate formation temperature.

Kinetic inhibitors are adsorbed on the surface of hydrate micro crystals, and micro dispersed droplets of water are absorbed in the flow of a fluid. Unlike thermodynamic inhibitors, kinetic inhibitors do not lower the hydrate formation temperature, but inhibit the process of hydrate formation. Kinetic inhibition is a temporary inhibition and is effective in producing and transporting hydrocarbons.

Chemical Methods of Combating Wax:

Wax remedial treatments often involve the use of solvents, hot water, the combination of hot water and surfactants, or hot oil treatments to revitalize production. Eight methods are obtainable for moving of wax, paraffin, and asphaltene:

• Hot fluid, Solvents, Dispersants , Crystal modifiers, A combination of the above, SNG (or NGS, nitrogen generating system) thermo-chemical cleaning, Microorganisms, Pour Point DepressantsSolvent treatments of wax and asphaltene depositions are the most successful remediation methods, but are costlier. There-fore, solvent remedy methods are reserved for applications where hot oil or water methods have achieved little success. When solvents connect the wax, the deposits are dissolved until the solvents are saturated. If they are not separated after saturation is extend, there is a strong possibility that the waxes will precipitate (re-crystallize), resulting in a situation more acute than that prior to treatment.

Dispersants do not dissolve wax but scatter it in the oil or water through surfactant action. They split the modifier polymer into smaller fractions that can mix more willingly with the crude oil under low shear conditions.

During the course of the project the performance of the pour point depressants were evaluated.

Pour Point Depressants

Pour point:

The pour point of a liquid is the temperature under which the liquid forget its flow characteristics.

Pour point depressants:

A pour point depressant lowers that temperature. Pour point depressants (also known as PPDs) are polymers that are designed to control wax crystal formation in lubricants resulting in lower pour point and improved low temperature flow performance.

Need of pour point depressants:

During pipeline transport of waxy crude oil, paraffin precipitation gives rise to several challenges that includes gel formation and wax deposition which has adverse impact on pipeline performance. Small dosages of polymeric wax or pour point depressants comprise an effective preventative measure.

Structural Character of Pour Point Depressants:

Most pour point depressants contain two basic components: polar components and nonpolar components. Nonpolar components are normally long alkyl chains which interact with paraffin waxes via nucleation, adsorption or co-crystallization. Polar components, such as esters, vinyl acetates, maleic anhydrides or acrylonitrile may interrupt wax crystal growth, modulate morphology and inhibit formation of large wax crystals.

Mechanism of Pour Point Depressants:

The additives are known to correctarrangement (size and shape) of wax crystals through the interaction with paraffin waxes. Thereby, the movement of wax crystals to form three-dimensional networks is stopped. The final effect is the improved macroscopic rheology of waxy crude oils. This can be achieved through surface adsorption and co-crystallization.

Interaction between PPDs and Paraffin Waxes:

Nucleation: At temperatures well above the WAT, certain polymeric wax inhibitors and PPDs self-assemble into micelle-like aggregates exhibiting a crystalline core and soluble hairy brushes surrounding the core, creating a larger number of sub-critical size wax nuclei (so-called polynucleation).

Adsorption and Co-Crystallization: At temperatures near or below the WAT, many polymeric wax inhibitors and pour point depressants co-crystallize with wax molecules or adsorb on growing surfaces of precipitated wax crystals. Incorporation of PPDs into wax crystals disrupts growth, inhibiting wax deposition and improving flow ability.

Solubilisation: At temperatures slightly above WAT, polymeric wax inhibitors and PPDs may interact favourably with soluble wax in the oil due to favourable van der Waals interaction between paraffin chains and long alkyl components. The solubility of paraffin waxes in oil is somewhat improved in the presence of wax inhibitors and PPDs, causing reduction in WAT.

III. Experimental

Evaluation of Efficiency of Pour Point Depressants

The pour point of the crude oil sample is measured according to method IP441. Oil samples were collected from different wells of western onshore. Composite crude was prepared by mixing crude oils collected from different wells of same field. The composite crude oil is then dehydrated using suitable demulsifier. Dehydrated crude oil (having minimum amount of water) is taken into reagent bottles to carry out PPD studies. Each reagent bottle used for studies contains same volume of crude oil.

Studies has been carried out in two phases.
1st phase: Screening of products at 1000 ppm dose.
2nd phase: Evaluation of screened products at 1000, 2000, 3000 and 4000 ppm dose.

Procedure:

Equal volume of crude oil was taken into reagent bottles and dosing and curing of crude oil sample was carried out.Oil samples (in reagent bottles) were preconditioned at 60 ^{o}Cfor 30 minutes in water bath.Then oil is dosed with 20% solution of products at desired concentration and 50 shakes were given to mix the product and oil homogeneously.Then curing of samples is done at 60 ^{o}C for 30 minutes and finally samples were taken out of water bath to evaluate pout points and viscosity.

For final evaluation, crude oil sample is taken in duplicates (Set 1 and Set 2). And same treatment is given as described above.
Set 1 contains: 2 blank and 3 treated (dosed with PPD), for day 1 study
Set 2 contains: 2 blank and 3 treated (dosed with PPD), for day 3 study (i.e. after 72 hours)

Set 1 samplespour point and viscosity reading are taken on the same day and set 2 samples are kept as such at room temperature for three day before readings are being taken.

Viscosity Measurement:

Viscosity measurement was also done on the oil sample to evaluate the performance of the pour point depressants.Viscosity is inverse measurement of the ability of substance to flow. Greater the viscosity of the fluid the less readily it flows.

Viscosity = Shear Stress/ Shear Rate

The viscosity measurement was done using Rheometer at 10/s shear rate and at 30^{o}C.

IV. Results & Discussion:

Table No. 1.1: Physico-chemical characterisation of crude oil

Parameter	Methods	Unit	Result
Density@15^{0} C	IP-160	Kg/l	0.9523
Specific gravity	IP-200	-	0.9528
API Gravity	-	-	17.01
Pour point	IP-144	^{o}C	39-42
Wax content	UOP 46:85	%	10.92
Saturate content	Wt. / Wt.	%	39.55
Aromatic content	Wt. / Wt.	%	33.75
Resin contents	Wt. / Wt.	%	22.22
Asphaltene contenT	Wt. / Wt.	%	4.68

Table No.1.2: Evaluation of PPD/ Flow improvers on Crude oil, Total Products = 26

S. No	**Particular**	**Details**
1.	Water content	4%
2.	Volume of crude oil	200 ml
3.	Doping Temperature	60 °C
4.	Curing Temperature	60 °C
5.	Curing Time	30 minutes
6.	Blank pour point	39 °C
7.	Dose of PPD	1000 ppm

S.N.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Products	A	B	C	D	E	F	**G**	**H**	**I**	J	K	L	M	N	O
Pour point °C	39° C	39° C	36° C	39° C	36° C	39° C	39° C	36° C	36° C	39° C	39° C	39° C	39° C	36° C	36° C

S.N.	16	17	18	19	20	21	22	23	24	25	26
Products	P	Q	R	S	T	V	U	W	X	Y	Z
Pour Point°C	39°C	39°C	39°C	39°C	39°C	39°C	39°C	39°C	39°C	39°C	39°C

Table No. 1.3: Evaluation of PPD/ Flow improvers on Crude oil at different doses, Total Products = 15

S.N	Products	Dose (ppm)	Observed pour point °C	Reduction in pour point °C
	Blank	**--**	**39**	**--**
1.	A	1000	39	0
		2000	39	0
		3000	39	0
		4000	36	3
2.	B	1000	39	0
		2000	39	0
		3000	39	0
		4000	39	0
3.	C	1000	36	3
		2000	36	3
		3000	36	3
		4000	36	3
4.	D	1000	39	0
		2000	39	0
		3000	36	3
		4000	33	6
5.	E	1000	36	3
		2000	36	3
		3000	33	6
		4000	33	6
6.	F	1000	39	0
		2000	36	3
		3000	36	3
		4000	33	6
7.	**G**	1000	39	0
		2000	39	0
		3000	36	3
		4000	33	6
8.	**H**	1000	36	3
		2000	33	6
		3000	33	6
		4000	30	9
9	**I**	1000	36	3
		2000	36	3
		3000	33	6
		4000	30	9
10.	J	1000	39	0
		2000	39	0
		3000	39	0
		4000	36	3
11.	K	1000	39	0
		2000	39	0
		3000	39	0
		4000	39	0

12.	L	1000	39	0
		2000	36	3
		3000	36	3
		4000	33	6
13.	M	1000	39	0
		2000	36	3
		3000	36	3
		4000	33	6
14.	N	1000	36	3
		2000	36	3
		3000	33	6
		4000	33	6
15.	O	1000	39	0
		2000	36	3
		3000	36	3
		4000	33	6

Table No.1.4: Evaluation of Efficiency of Pour Point Depressants

S. No	**Product name**	**Dose in ppm**	**Pour points of 1st day& 3rd day**	
			0 Hours	**72 Hours**
1.	**H**	4000	30 °C	33°C
2.	**I**	4000	30 °C	33 °C
3.	**G**	4000	33 °C	36 °C
4.	**Blank- 1**	Untreated	39 °C	39 °C
5.	**Blank-2**	Untreated	39 °C	39 °C

Table No. 1.5: Viscosity @30°C for day 1

Blank 1	**H**	**I**	**G**
9532	569.3	680.2	965.1
9215	577.6	691.4	979.9
9031	588.6	705.3	989.7
8918	596.6	699.9	997.1
8841	609.0	701.2	1012
8715	615.5	706.6	1016

Table No.1.6: Viscosity @30 °C for day 3

Blank 2	**H**	**I**	**G**
14700	5570	3837	2310
14560	5455	3787	2268
14510	5371	3753	2239
14460	5313	3724	2207
14370	5237	3701	2183
14300	5183	3686	2162

Discussion:

Crude oil sample was collected from different wells of Western Onshore field and the mixture was used for the evaluation of Pour Point Depressant. Physiochemical parameters have been depicted in Table - 1.1, which reveals that crude oil has very high pour point of 39-42°C. A high wax content and asphaltene content clearly indicates that transportation of crude oil will be a big challenge during winter.

Total 26 number of pour point depressant(PPD) were studied. However no product was effective at a dose of 1000 ppm (Table - 1.2). Accordingly, Only 15 products were further evaluated at 2000, 3000, and 4000 ppm dose as shown in Table - 1.3. Out of these 15 products, only three products were effective that too at a very high dose of 4000 ppm. The products, Product G, Product H & Product I were effective in depressing the pour point upto 30-33°C.

Transportation of crude oils depends heavily on pour point and viscosity of the crude. To study the effect of PPD on crude oil, Rheological studies were also carried out for these three products.

It was observed that all the three products (Product H,I & G) were effective and were reducing the viscosity from app 9000 to 600 cps (Table - 1.5).Drastic reduction in the viscosity clearly indicates that the Products are not reducing the Pour point considerably but are very effective in terms of viscosity reduction which in turn will help in the smooth flow of the crude oil.

However the viscosity increases 3-10 times from day 1 to day3 (Table 1.5 & 1.6). Field experience of these crude oils indicates that the field trial of these three products for seven days must be carried out to get the real time picture of these products.

V. Conclusions:

High pour point and high wax content along with high density indicates the crude oil is heavy in nature.
High asphaltene content also indicates that heavy oil along with high pour point will create number of specific transportation problems.
Three products are quite effective in reducing the viscosity. Field trial for seven days must be carried out to get the required data which can help to find the best product.
At the onset of winter dosing must be done in advance to control any transportation problem.

In case of any eventuality Xylene, Toluene or light oil must be kept ready to solve the transportation problem.

VI. Acknowledgement:

Authors would like to convey their sincere thanks to the management of Parul university for allowing to carry out research work.

Authors would like to convey their thanks to HOD for her constant encouragement.

Authors are also grateful to the principal of PIAS for his efforts and encouragement throughout the course of studies.

Authors would also like to convey their gratitude to the premier oil company for allowing and providing necessary facilities to carry out this work.

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