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Flow Improvement of a Waxy Crude Oil by Chemical Additive Utilization

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Abstract: The pipeline transportation of waxy crude oils at temperature below their natural pour point carries the risk if the pipeline is shut down and the oil cools statically, an interlocking wax crystals structure can be formed, which could prevent the restart of the line. The addition of additives to waxy crude oils improves their fluidity. This study summarizes the use of five different pour point products at different concentrations to waxy crude oil named K.

Key words: Paraffinic crude, wax deposition, pipeline transplantation, rheological behaviour, flow improvers

INTRODUCTION

The continuous flow of crude oil is a vital factor for the economy of a country. However, the presence of paraffins ($>C_{20}$) in a crude oil can cause major economic problems if wax precipitation allowed occurring during the production at any point of surface facilities (Fig. 1). At sufficiently high temperature, all paraffins are completely dissolved in oil and are in a thermodynamic state balance. The oil has Newtonian behaviour. If at any point between the well head and storage tank, the balance is broken, by a change in the temperature or/and pressure, or by losses of volatile gas[1], paraffins can crystallize and precipitate. Technical remediation techniques may not even be applied until wax deposition occurs. Prediction and identification of the eventual deposit problems would permit to avoid losses of time and money. This study presents a case of Tunisian crude oil K, transported through 125 km long pipeline. During five months, we observe a serious paraffin deposit removed by pigging. But, this mechanical method was not sufficient in cold period where pigging becomes frequent (one by week). A more cost effective method of handling the paraffin is using chemicals to prevent paraffin deposition. Five products were tested, based on the knowledge of the physical properties and the rheological behaviour of the oil K.

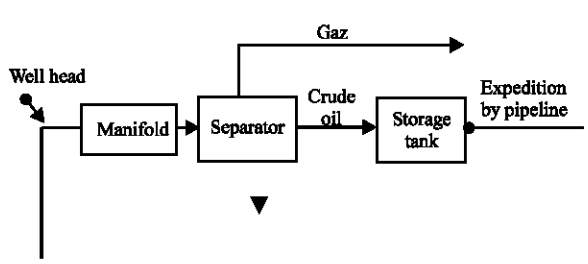

Fig. 1: Deposit localisation

Waxy crude oils characterisation: Waxy crude oil can be defined on the basis of a few conventional analysis such gravity according to the ASTM D1298[2] and kinematic viscosity according to ASTM D445[3]. These analyses are not sufficient for rheological behaviour characterisation. In order to have more information, we proceeded for some other measurement:

Pour Point (PP): A first characterization of waxy crude oils is by measuring the PP which is related to the temperature at which the oil is observed to flow when cooled under prescribed conditions. The used method is the ASTM D97[4]. Contrary to a physical property such as melting of a pure substance, the PP of a waxy crude oil is strongly dependent of the procedure applied prior to and during measurement. Since they're different types of PP are determined:

- The maximum PP implies heating oil to 45°C. At this temperature, the distillate paraffins dissolves but not the microcrystalline paraffin. After heating to 45°C, the crude oil is cooled to 35°C; afterwards it is cooled until the PP is reached.
- The minimum PP is reached when oil is heated to 105°C. At this temperature, all paraffins have been dissolved. The crude oil is then cooled at room temperature to 35°C and then cooled normally until the PP is reached.

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Table 1: Comparison between two oils

Oil	Density 15.6°C	PP
TS9	0.920	-27
ZA2	0.832	-33

Table 2: Characterization of crude oil K

Method	Method	K oil	Unit
Density at 15°C	ASTM D-1298	838.00	kg m^{-3}
Water content	ASTM D-4006[10]	0.60	Vol/Vol (%)
Kinematic viscosity at 40°C	ASTM D-445	4.70	Cst
PP	ASTM D97	18.00	°C
Cloud point	ASTM D2500	36.00	°C
Paraffin's content	UOP 46-64	9.40	mass (%)
Asphaltenes content	IP 143	0.35	mass (%)

Higher PP is not synonymous of heavy oil. A certain number of light and averages oils exhibit a higher PP[5]. Cases presented below of two oils (Table 1) are an example, since oil TS9, which density classified among the heavy oils, shows a very low PP, whereas oil ZA2, considered as being light and exhibit a very high PP. In fact, the value of PP is reliably to its composition.

Paraffin's content: In the terminology of petroleum industry, paraffins designate any organic fraction that precipitate to form deposits or agglomerates. The analytic method defines the paraffin content of oil, which is analysed according to the standard method UOP 46-64[6]. This method involves diluting the crude in a suitable solvent, cooling down (-30°C), filtering and weighing.

Cloud point: As long as the crude oil is at sufficiently high temperature, all wax will be completely dissolved in the oil. Upon cooling, a temperature will be reached at which the first paraffin crystal appears. Below this temperature, more and more wax will crystallise with decreasing temperature. The used method for this measurement is the ASTM D2500-66[7]. This determination is difficult for black oils since it is based on the observation[8].

All analyses on oil K have been made on a representative sample of the fluid produces. The sampling was done before the manifold between the wellhead and the separator (Fig. 1). The oil was at 63°C and maintained at 40°C in the laboratory and kept at this temperature during all the study.

Analytic results: The physical characteristics of K crude oil results suggests that K have light range API gravity (39°), contains significant quantities of paraffins that confer him paraffin character (9.4%) (Table 2). The asphaltene content by IP 143[9] is not enough important to influence its flow behaviour. Another interesting parameter is the cloud point. Above this temperature, which is equal to 36°C for K oil, crude cannot experience wax problems of any sort. Below the cloud point, the probability of wax deposit increases.

Rheological properties: The most efficient way for transport of large volumes of crude oil is by pipeline. The operator can be confronted to difficulties relatives to the oil properties themselves. In fact, some oils have a viscosity that is independent of flow velocity. Such behaviour is Newtonian. A waxy crude oil in contrast, has a shear rate dependant viscosity. If during transport through the pipeline, the crude oil will cool down, paraffins will crystallise and non-Newtonian effects will become apparent. Various studies have been done on the subject mass[11-13]. The knowledge of rheological oil properties under certain conditions of shearing and at known temperature, constitute the best approach to decide the choice of the preventive treatment to adopt. Three parameters are required: the viscosity under shearing, the restart pressure and the quantitative paraffin's deposit.

Viscosity under shear: At low temperatures, the viscosity of waxy crude oils depends on the shear rate. During flow, a shear force is applied that in addition to visco-elastics effects, may breakdown the interlocking crystals making the viscosity time dependent as well. Effects on the dynamic viscosity of oil K have been measured under a constant shear during the cooling of the oil until a supposed minimal temperature. Before testing, the following thermal profile has been applied to the oil K: Crude oil taken from storage temperature at 35°C, heated to 105°C to bring it in its minimum conditions, cooled to 63°C at a rate of 40°C h^{-1}, doped or not at this temperature, cooled to 40°C by leaving it on the table at ambient for a few minutes, then the preheated Haake Rot viscometer cup (40°) was filled and cooled to 2°C at a rate of 30°C h^{-1}. In this case, the calculated shear rate is equal to 33 s^{-1}, which is equivalent to movement of 15000 bbl/day.

The analysis of the curve shows that in dynamic conditions, the viscosity of the oil begins to increase quickly with the reduction of the temperature; this being due to the crystallization of paraffins whose quantity is especially more and more important surroundings of the pour point (Fig. 2).

Restart pressure: Among its severely flowing characteristics, waxy crude oil can normally be pumped. However, some external parameters can interrupt the normal flux[14-15] as pump failures, lines damages or storage limitations. During such an unscheduled shutdown the crude is cooled in static conditions. This will conduct to

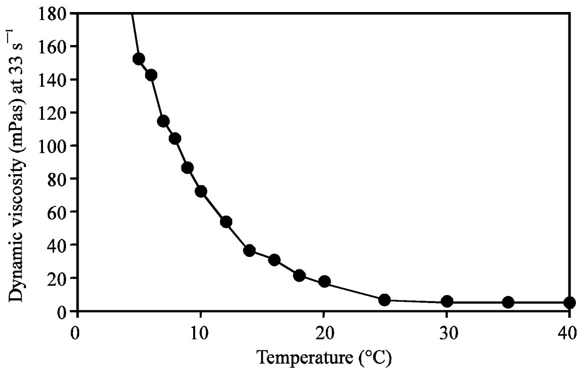

Fig. 2: Dynamic viscosity of the oil K without additives

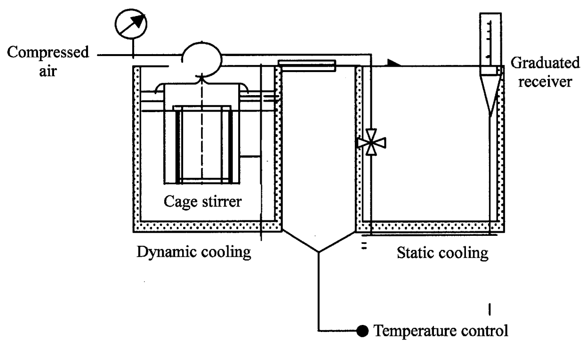

Fig. 3: Model pipeline simulator

the formation of an interlocking crystal network[16]. Restart of the gel will depend on the available shear stress, related to the pump pressure and the line dimensions. If the available shear stress is less than the yield stress of the oil, the gel structure will not be broken and the restart becomes impossible. It requires the increase of the shear stress or alternately, a reduction of the yield stress by applying heat or solvents. Different models of pipeline have been developed by various companies as BP, ESSO, CONOCO[17]. SHELL for its part uses a model that simulates the conditioning of oil during the flow and the shutdown. Experimentally, the oil is introduced in a cage with stirring, to simulate the turbulent movement of the line and it's cooling in dynamic conditions. The crude oil is then transferred to a 16 m pipeline in which the static cooling until restart temperature, followed by shutdown is simulated. Then, a shear stress is applied and increased until the yield stress is reached, evidenced by a small flow. The selected cooling conditions for oil K are based on a representative profile of really conditions in the field:

The crude was taken from storage at 40°C, heated to 105°C to bring it in its minimum conditions, cooled dynamically to 63°C at a rate 40°C h^{-1}. At this temperature, the oil is placed in the dynamic part of the pipeline simulator and a new temperature profile is applied: cooling to 41°C at a rate of 22°C h^{-1} and 23°C at a rate of 13°C h^{-1}. At 23°C, the oil is transferred in the static part of the pipeline simulator, cooled gradually over a period of 84 h to the chosen restart temperature of 3°C.

For the 125 km pipeline used here with an internal diameter of 0.203 m, the required pressure for restarting the oil K at 3°C can be calculated according to the formula[14]:

$$Pr = 4 * \tau * L/D \quad (1)$$

- Pr is the required restart pressure in Pascal (Pa)
- τ is the yield stress as measured in the experiments (Pa)
- L and D are respectively the length and the internal diameter expressed in meters (m).

For the oil K, the measured yield stress is equal to 30. Minimum required pressure of 700 for the undoped crude oil was found at 3°C. When this is compared with the available restart pressure in the field of 97 bars, we conclude undoped crude oil could not be restarted after shutdown.

Wax deposition: When the oil temperature is lower to its trouble point, paraffin crystals begin to precipitate. These deposits took place at any level of the production facilities (tubings[18], production lines, separators, storage tank, pipeline…). Wax deposition on the pipe walls limits the pumping of waxy crude oil. The deposits may vary from soft to hard, from yellow to black and consist of a mixture of wax, oil, asphaltenes and inorganic material. To examine wax deposition of oil K, we used the method adopted by Shell: Cold Finger Test (CFT). It assesses the amount of wax deposited on a cooled thimble inserted in the oil. At the end of the test, the capillary is drained, the deposit weighed and its composition analysed.

The risk of wax deposition from the warmer crude oil K on the colder pipeline (125 km) was assessed by carrying out the experiments on pure K. The profile of temperature is described below: the oil was heated in a metallic container to 105°C, kept there during 20 min and cooled to 63°C at 40°C h^{-1}, kept for 5 min on table and then the cold finger test cup, which was held at 40°C, was filled and kept at this temperature (under stirring) during the test. The CFT, held at 10°C, was immersed in the oil for 2.5 h. The amount of wax clinging to the CFT was measured, dissolved in warm toluene, collected, dried and weighed. Amounts of hard wax found for oil K was equal to 1880 mg.

Table 3: Results of restart ability at 3°C

Additive concentration (ppm)	Oil K	100 SS	150 SS	200 SS	150 SV	150 AC	100 CC	150 PT
τ (Pa) yield stress at 3°C	30	1	1	1	1	18	1	4
Require pressure (Bars)	739	25	25	25	25	443	25	90.5

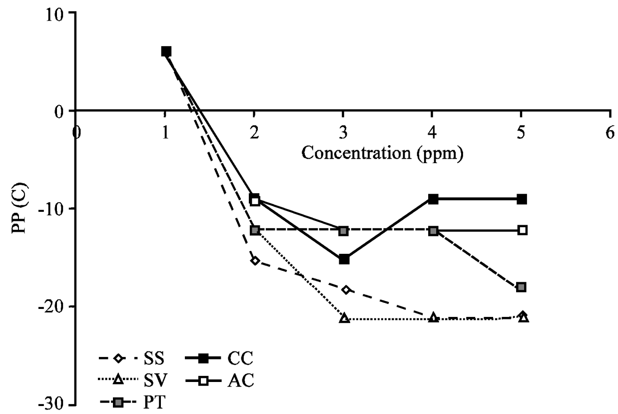

Fig. 4: Evolution of the PP according to the concentration of the additive

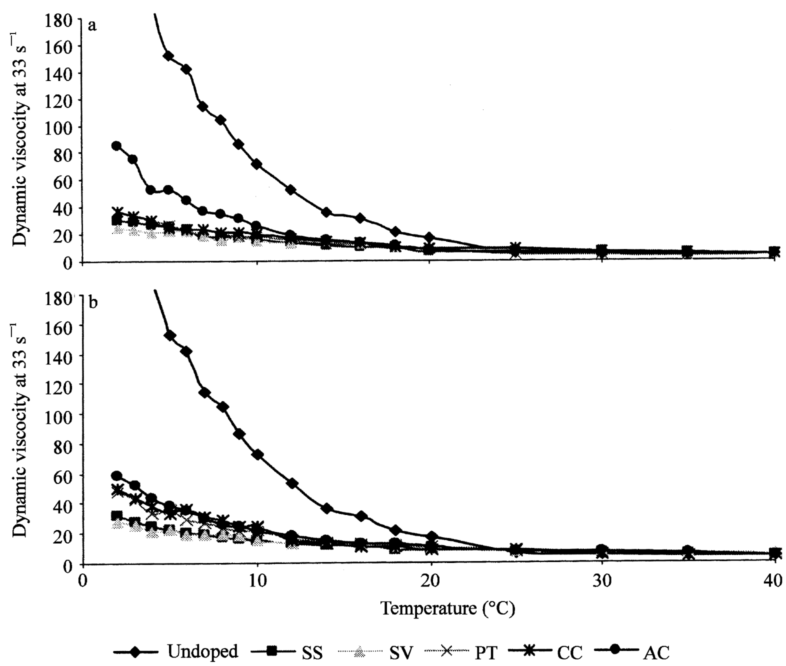

Fig. 5: Dynamic viscosity; 5a: 100 ppm, 5b: 150 ppm additive rate

Chemical treatments: In the aim to improve the flow properties of waxy crude oil, the addition of chemicals will allow the operator to transport oil at lower temperatures than its PP. Crystal modifiers or flow improvers are used to prevent paraffin deposition by lowering the PP and reducing the viscosity. In the case of line shut down and static cooling, these additives must have the property to decrease the yield stress and dynamic viscosity[19-21]. Therefore, the waxy crude oil can be pipelined on long distances and stored. In all cases, the efficiency of the additive will depend on:

Thermal history: It is well known that heat treatment to which the oil has been subjected influences its fluidity[16]. Temperature is the most factors influencing the physical and rheological properties of waxy crude oil. To be realistic, a temperature profile must be applied in all tests.

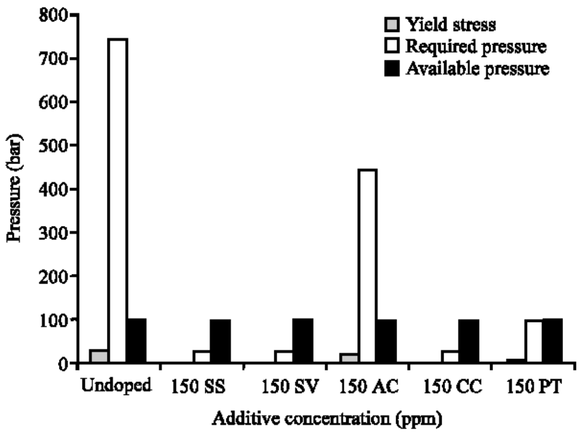

Fig. 6: Effects of additives on K restart ability

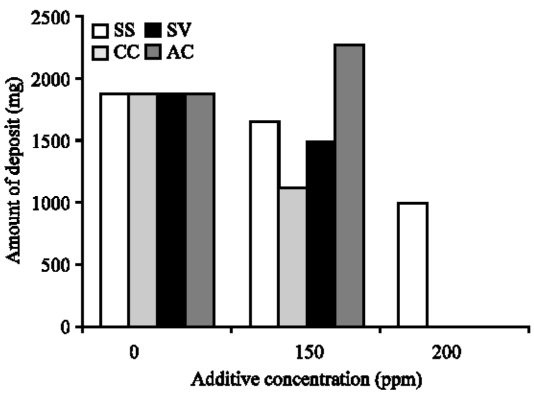

Fig. 7: Effect of additives on wax deposit of K

Crude oil properties: A chemically paraffin prevention program is generally based on a good knowledge of exact nature of crude oil to be treated. Thus permits a more cost effective method for preventing deposition[22].

Doping temperature: The efficiency of additive is greatly influenced by the temperature of the oil at the injection point. This factor must be taken into account in the laboratory experiments.

Effects of chemical additives named SS, CC, SV, AC and PT on oil K are studied. They are polymeric compounds as presented by Chanda[23].

PP response to additives: Based on some indications from the field, we adopt the temperature profile described below: the sample was taken from storage at 35°C, heated to 105°C to bring it in its minimum conditions, cooled to 63°C which is the inlet temperature in the pipeline at a rate of 40°C h^{-1}, treated at this temperature and cooled according to the ASTM D97-66. For injection rate varying between 75 to 200 ppm, we note a very good response for all the additives. The PP value for oil K decreases from +12°C to -21°C (Fig. 4).

Effects on the dynamic viscosity: Dynamic viscosity effects were measured under constant shear during cooling of undoped crude oil to 3°C. Before starting tests, a similar thermal profile for pure crude was applied. The obtained data shows that under dynamic conditions, viscosity increase is very limited (Fig. 5a and b).

Effects on restart ability: Restart ability tests have been conducted in the model pipeline on the oil treated with 100, 150 and 200 ppm of SS; 150 ppm of SV, 150 ppm of AC, 150 ppm of CC and 150 ppm of PT with the same temperature profile for pure K (Table 3).

The required restart pressure can be calculated according to the formula (1). The required restart pressure at 3°C is reduced to 25 bars, the quarter of the available pressure on the line in the field (Fig. 6).

Effects of additives on wax deposits: The risk of wax deposition from crude oil on the colder pipeline wall was assessed by carrying some experiments on K oil in a Cold finger test, in presence of 100 and 200 ppm of additives. The temperature profile for pure K was applied.

Results show clearly that the amount of wax deposited on the cold finger can be reduced by the utilization of a certain quantity of chemical additives. The quantity of deposited wax in the pure oil K was reduced to 990 mg in presence of 200 ppm of SS product and to 1480 mg with 150 ppm of SV product (Fig. 7).

The results of this study can be summarized in five points:

- The characterization of the oil K showed the existence of minimum and maximum PP. Such behaviour is due to its paraffin's content;
- Flow behaviour of the oil K is deteriorating as the cloud point temperature is reached (36°C). The transport of the oil through the 125 km long pipeline can benefit considerably from the use of additives by improving the PP response.
- The dynamic viscosity behaviour during cooling from 40 to 2°C at constant shear rate (33 s^{-1}) calculated to be typical in the field is significant of a Non-Newtonian fluid. The crude doped with 100 and 500 ppm of additive SSS, SV, CC, PT and AC retained a very low dynamic viscosity, up to 70% lower than for undoped crude.
- Simulated pipeline flow behaviour of oil K in a model of pipeline with restart temperature of 3°C, showed a great improvement in required restart pressure, the yield stress decreased from 30 to 1 Pa with use of only 150 ppm of SS, SV or CC. This means, knowing that the available pressure in the field is 97 bars, that with 150 ppm of any of the 3 best products, restart pressure is approximately 25% of the available pressure.

- The effect of the SS, SV and the CC products on wax deposition on the cold pipeline wall was simulated using the cold finger test; the crude oil was at 40°C and wall temperature at 10°C. The results obtained have shown a deposition reduction of 47, 40 and 21% using, respectively SS (200 ppm), CC (150 ppm) and SV (150 ppm) products.

This work permitted:

- To reveal some major problems of the exploitation of the waxy crude oil K. There are:
  - Higher viscosities
  - Higher shear stress for restart
  - Paraffin's deposits on surfaces facilities
- To improve the fluidity of oil K by improving its physical and rheological properties and to avoid production shutdown by using flow improvers at a medium injection rate.
- To decrease the quantity of wax removed by pigging.

A good knowledge of the nature, the physical and chemical properties and the rheological behaviour of the produced fluid, are necessary to prevent deposit problems.

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