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INFLUENCE OF SHEAR HISTORY ON RHEOLOGICAL BEHAVIOR AND CRYSTAL MORPHOLOGY OF WAXY OILS

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Abstract. *The pipelines used in the production and transportation of waxy crude oils are in contact with the ocean floor at approximately 4 °C. The interruption of the crude oil flow may cause the oil gelation. The wax crystallization is the responsible for this phenomenon that becomes one of the major problems in production and transportation of waxy crude oil. Pressures required to break up the gel and restart the flow are increased in large proportions. The literature shows that this gelled structure is highly influenced by the thermal and shear histories. The influence of shear rate during cooling on the gel strength and on the morphology of paraffin crystals is investigated in this paper. The evaluation of these effects is based on rheological experiments performed with dynamic cooling. Moreover, the visualization of microscopic structure of the crystal was possible with the Rheoscope™ system coupled to the rheometer. The results show that higher shear rates the lower the gel strength. It can also be anticipated that the size of wax crystals formed are smaller when a shear rate during the cooling is applied then the crystals precipitated in a static cooling.*

Keywords: *Wax crystallization, Rheological Experiments, Shear history, Gel Strength, Crystal morphology.*

1. INTRODUCTION

The reservoirs of waxy crude oils are located in deep and ultradeep water. These materials are composed mainly by hydrocarbons and some heteroatoms (Sadeghazad et al. 2000; Venkatesan et al. 2003). In the reservoir condition, i.e., high temperatures (60~150 °C) and pressures (50-100 MPa) all the components are dissolved in the oil (Venkatesan et al. 2005) and the material behaves as Newtonian fluid (Pedersen and Rønningsen 2000; Andrade et al. 2015). The pipelines used in the production and transportation of crude oils are in contact with the seafloor that is at approximately 4 °C. The material loses heat to the environment, the solubility of the wax in the oil decreases and below the crystallization temperature waxes precipitate as solid structures (Andrade et al. 2017a). The wax crystallization provides a non-Newtonian behavior to the material and when the production is interrupted the crystals can entrap the oil leading to a gel-like structure to the material (Aiyejina et al. 2011; Oliveira et al. 2012).

Pressures higher than the usual are required to break-up the gelled structure and to resume the flow. The start-up pressure is related to the material gel strength. In turn the rheological characteristics of the gelled oil are influenced by the thermal and shear histories that were imposed on the material. The macroscopic behavior of the material is related to the quantity, morphology and size of the precipitated crystals (Smith and Ramsden 1978; Geri et al. 2017). The influence of the cooling rate on the crystals characteristics and on the macroscopic behavior of a model waxy oil was studied in a recent paper (Andrade et al. 2017b). The authors showed that for a static cooling the higher the cooling rate the lower the crystals length. On the other hand, a non-monotonic behavior was observed when the critical stress and the dynamic moduli were analyzed as a function of the cooling rate. It is worth mentioning that this same non-monotonic behavior was already reported by Lee et al. (2008), but the microscopic analysis proposed by Andrade et al. (2017b) provided interesting insights and conclusions relating the wax morphology and the macroscopic behavior of the gelled material.

The effect of the shear during the cooling was already reported by many authors (Davenport and Somper 1971; Rønningsen et al. 1991; Wardhaugh and Boger 1991; El-Gamal 1998; Singh et al. 1999; Webber 1999; Kané et al. 2003; Venkatesan et al. 2005; Lin et al. 2011). The majority of the authors state that the higher the shear rate or the shear stress imposed during the cooling the lower the material gel strength. Venkatesan et al. (2005) observed that the material yield stress increases with the shear stress applied during the cooling for low values of shear stress. The opposite behavior was presented by high values of shear stress imposed during the cooling, i.e., the higher the shear stress the lower the material gel strength. In other words, the shear stress presented a non-monotonic influence on the macroscopic behavior of the model waxy oil studied in their work.

In order of relating the influence of the shear history on the crystal morphology and on the macroscopic behavior of waxy oils, in the current paper different shear rates are imposed during the cooling of a model waxy oil and the analyses are performed by means of rheometric and microscopic experiments.

2. MATERIALS AND METHODS

The rheological experiments of this present study were conducted using model wax-oil system. The formulated oil was prepared with 5% (by weight) of paraffin wax (Sigma Aldrich 327217 Cas-No: 8002-74-2) in mineral oil (Sigma Aldrich 330779 Cas-No: 8042-47-5). As reported by Andrade et al. (2017a) the thermodynamic solid-liquid temperature of this specific oil is 32 °C.

The rheometric experiments were performed in triplicate on the rotational rheometer, Haake Mars III (Haake Co., Germany) with a minimum torque of 5.10^{-8} Nm. The test temperature was controlled by a Peltier electronic system, aided by a thermostatic bath. The rheometer was equipped with serrated-parallel plates with 35 mm diameter and gap of 1.0 mm.

The microscopic images were obtained by means of commercial equipment coupled in the rheometer, named as Rheoscope™. The system is equipped with a 20x lens, resolution of 1 μm and a Black-and-white 'progressive' scan CCD camera with 1024x768 pixels. An upper polished parallel plate with 35 mm diameter was used in these experiments to reflect the light from the Rheoscope™ system and then allowing the visualization.

Before each experiment, a pre-treatment was realized by heating the sample in a closed bottle at 50 °C for 30 minutes in an oven for the complete dissolution of paraffin in oil. A specimen is then loaded in the rheometer that is already at 50 °C, the upper plate is placed in the measurement gap and all the system is kept in this temperature to guarantee thermal homogenization. Experiments were performed with a static and dynamic cooling from an initial temperature of 50 to 4 °C, with a constant cooling rate of 1 K/min. After this step, the specimen was maintained aging for one hour and then an oscillatory stress-sweep test started to determine the critical stress of the material. Shear rates evaluated during the cooling and all the experimental procedure are detailed in Table 1. The other parameters cited were maintained constant in all experiments.

Table 1. Experimental procedure for the analysis of waxy oil

	Rheometric Experiments	Microscopic Experiments with Rheoscope™ system coupled
Initial cooling temperature	50 °C	
Test temperature	4 °C	
Cooling Rate	1 K/min	
Static and Dynamic cooling	Shear rates of 0, 0.1, 1, 10, 100 s^{-1}	
Aging time at 4 °C	one hour	
Rotor type	Serrated parallel plates with 35-mm-diameter, gap of 1.0 mm	Polished parallel plates with 35-mm-diameter, gap of 0.55 mm
Analysis at the end of aging time	Oscillatory stress amplitude sweep, ω= 1 Hz, τ_i= 10^{-1} Pa, τ_f= 10^4 Pa, 30 points per decade	Images with a 20x lens, camera Black-and-white 'progressive' scan CCD, and 1 μm resolution

3. RESULTS AND DISCUSSION

In this section is analyzed the effect of the shear rate on the viscosity during the cooling, on the dynamic moduli in the linear viscoelastic region, on the critical stress after one hour of aging at 4 °C and on the morphology of the crystals.

3.1 Effect of shear rate on the viscosity

Figure 1 shows the apparent dynamic viscosity as a function of temperature during the cooling for different shear rates. As can be seen, from 50 °C until approximately 24 °C the material viscosity is independent of the shear rate,

consequently, the material is a Newtonian fluid. When a temperature of approximately 24 °C is reached, the viscosity values begin to increase differently for each shear rate applied. As proposed by Andrade (2017a) the temperature in which the precipitated crystals affect the material viscosity is called crystallization temperature, T_c. As explained in detail by the authors the crystallization temperature is lower than the highest thermodynamic solid-liquid equilibrium temperature, $T_{eq,SL}$, because of the supersaturation required for the beginning of the nucleation and growth of the crystals. The degree of supersaturation can be determined as $\Delta T_{sup} = T_{eq,SL} - T_c$. This metastable region width is function of the cooling rate, as already reported for this same model waxy oil (Andrade et al. 2017a) the higher the cooling rate the higher the ΔT_{sup}. In turn, theoretically the higher the mechanical stirring the lower the ΔT_{sup} (Mullin 2001; Nývlt et al. 2001), in other words, in the rheometric experiments the higher the shear rate imposed on the material the lower the crystallization temperature. On the other hand, the theoretical behavior was not observed in the current experiments. As can be noted, the change in the viscosity slope happens in the same temperature for all the cases analyzed, $T_c \sim 24$ °C. For this specific material, the degree of supercooling is affected by the cooling rate (Andrade et al. 2017a) but is not influenced by the shear applied during the cooling.

As can be noted in Fig. 1, the maximum apparent dynamic viscosity analyzed is present in the final cooling temperature for all curves. As also noted, the smaller shear rates applied, the higher the maximum viscosity at the final of cooling.

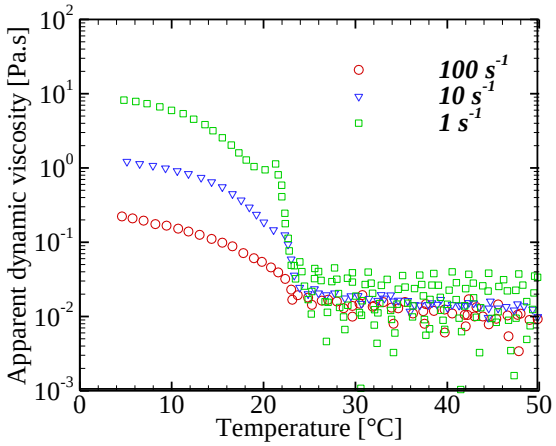

Figure 1. Apparent dynamic viscosity as function of the temperature evaluated at three different shear rates applied during the cooling.

3.2 Effect of shear rate on the gel strength

After the cooling and after one hour of aging time at 4°C, an oscillatory stress sweep experiment was performed to determine the dynamic moduli and the oil critical stress. At the beginning of the test the material has the storage modulus, G', higher than the loss modulus, G'', as a result of predominantly elastic behavior. When larger stresses are applied this behavior changes and G' crosses over G''. At this point, the critical stress was determined.

Figure 2a shows the storage and loss moduli evaluated at the beginning of the oscillatory test, in the linear viscoelastic region. As can be noted, the higher the shear rate imposed during the cooling the lower the dynamic moduli evaluated at 4 °C. For example, the storage modulus decreased two orders of magnitude when the applied shear rate was varied from 100 to 0.1 s^{-1} during the cooling. Therefore, the higher the applied shear rate during the cooling the larger the phase angle at 4 °C. This behavior shows that although after the aging time the material presents a predominantly elastic behavior in all the cases, at higher shear rates the viscous behavior can not be neglected.

The same experiment was performed with a static cooling. In this case, the dynamic moduli presented even higher values. The storage modulus, G', measured was 930000 Pa. The loss modulus, G'', presented a value of 120000 Pa. Lastly, the phase angle was 5.2 º. It is possible to note the dynamic moduli to a static cooling is approximately two orders of magnitude higher than the dynamic cooling performed with a shear rate of 0.1 s^{-1}.

The critical stress as a function of the shear rate is shown in Fig. 2b. As can be seen, the critical stress decreases with the increasing of shear rate applied during the cooling. As also noted, the critical stress in the smaller shear rate evaluated (0.1 s^{-1}) is more than ten times larger to the critical stress at 100 s^{-1}. In other words, the critical stress at a shear rate of 100 s^{-1} is approximately 1 Pa, while at 0.1 s^{-1} is more than 15 Pa.

In static cooling, the critical stress measured was approximately 500 Pa. As ca be seen, the difference between a static and a dynamic cooling is quite significant. The critical stress measured with a static cooling was one order of magnitude higher compared to dynamic cooling.

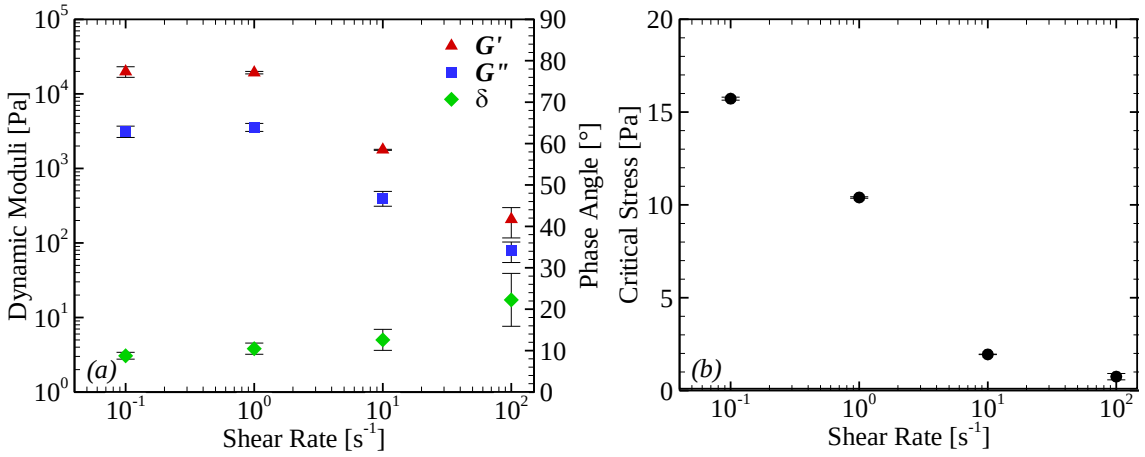

Figure 2. (a) G′, G″ and phase angle as a function of shear rate. (b) Critical Stress as a function of shear rate.

3.3 Effect of shear rate on crystal morphology

The same experiments experimental protocol was performed with the Rheoscope™ system. After the cooling and after one hour of aging time the images were obtained. Figure 3a shows the crystals after a static cooling (with no shear during the cooling). Figure 3b, Fig 3c and Fig 3d show the crystals after dynamic cooling performed with a shear rate of 1, 10 and 100 s^{-1}, respectively, and a cooling rate of 1 K/min.

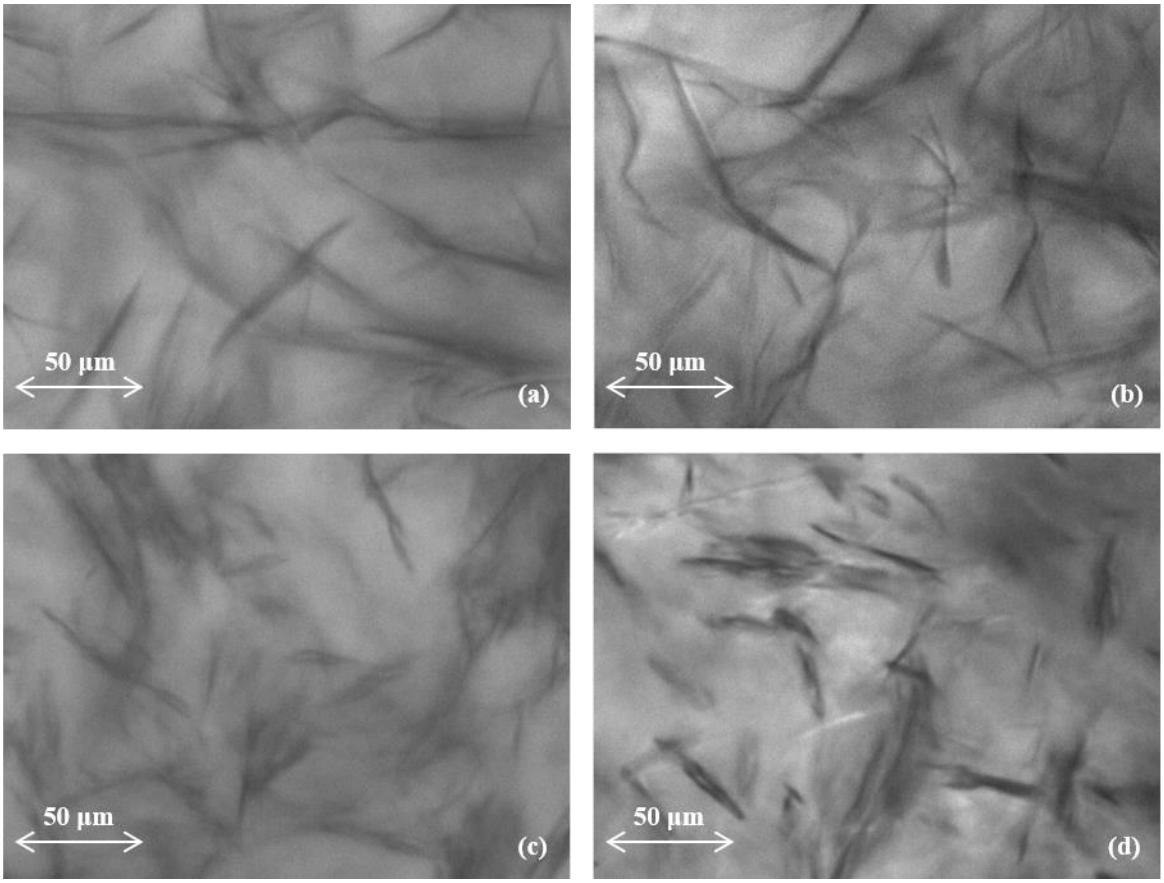

Figure 3. Crystal morphology at 4 °C after (a) a static cooling; a dynamic cooling with a shear rate of (b) 1, (c) 10 and (d) 100 s^{-1}, performed with the same cooling rate, 1 K/min.

It can be seen that the shear imposed affect the morphology of the crystals at the end of the cooling as shows Fig. 3. It is possible to note the crystals have a needle like structure in all cases, but the shear during the cooling lead to smaller crystals in the end of the cooling. However, the difference in crystal size in the end of the cooling is not very significant

when are compared dynamic cooling with shear rates of 10 and 100 s^{-1}, i.e., the crystals seem to be the same length in both cases. Also, can be noted that visually, in Fig 3a and Fig 3b, there are no difference between the crystal size after a static cooling and after a dynamic cooling with a shear rate of 0.1 s^{-1}.

The characteristic length, L_c, of the paraffin crystals are showed in Fig 4. Figure 4 shows the mean length obtained measuring ten different crystals for each shear rate applied, and for static cooling. It can be noted there is a tendency of the length of the crystals increases when smaller shear rates are applied, however, they are almost the same size when the error bar is considered, e.g., at the higher shear rate applied (of 100 s^{-1}) the L_c is approximately the same that the crystals cooled with a shear rate of 10 s^{-1}.

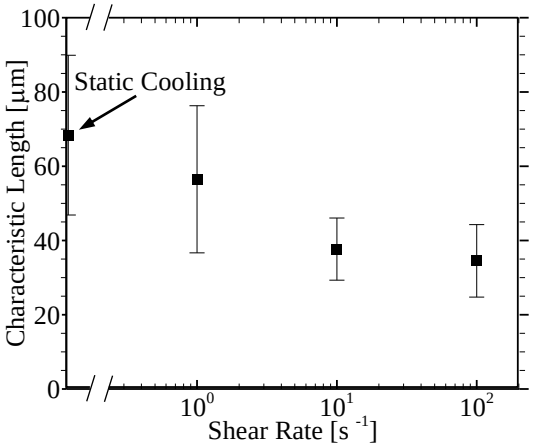

Figure 4. Characteristic Length of crystals as a function of shear rate evaluated at three different shear rates applied and static cooling.

3.4 Discussion of the results

It was shown that a shear rate imposed during the cooling can affect the nucleation of the crystals, the dynamic moduli and the critical stress required to break up the gelled structure. As mentioned in section 3.2, the higher the shear rate applied during the cooling, the lower the critical stress to break up the structure at the end of the cooling. An even more significant difference can be noted when are compared the critical stresses between static and dynamic cooling. The stress to break up the gel is at least one order of magnitude higher in a static cooling than when any shear rate is applied.

On the other hand, in the visualization tests presented in section 3.3, the crystals formed with no shear history have approximately the same length the crystals cooled with a shear rate of 1 s^{-1}. The difference showed in the rheological experiments after a static and after a dynamic cooling was not noted in the visualization tests. It is possible to conclude that not only the morphology and size of the crystals are the responsible for the macroscopic behavior of the material. Although there is an influence of the shear rate in the length of the crystals, the interaction between the crystals can also affect the behavior of this material.

4. CONCLUSION

In the current paper the influence of the shear history on the morphology of the crystals and on the macroscopic behavior of waxy oils is analyzed by means of microscopic and rheometric experiments. It could be seen that a shear rate imposed during the cooling can affect the behavior of this material. The main conclusions can be summarized as:

i) The shear rate influence on the nucleation and crystals growth;

ii) The higher the shear rate applied during cooling the lower the dynamic moduli in the linear viscoelastic region and the lower the critical stress required to break-up the gelled structure;

iii) The critical stress to break-up the gelled structure is one order of magnitude higher when the cooling was static than when a shear rate was imposed. Although it can be noted the critical stress is different for each shear rate evaluated, this difference is not verysignificant as when are compared these values with a static cooling;

iv) The shear during the cooling can affect the size of the crystals at the end of the cooling. Although there is a tendency of the length of the crystals being lower when higher shear rates are applied, the characteristic length is almost the same to the shear rates of 10 and 100 s^{-1} and for 1 s^{-1} and static cooling;

v) The length of crystals at the end of cooling is not the only responsible for the critical stress required to break-up the gelled structure. The interaction between the crystals also can affect the behavior of this material.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

Aiyejina A, Chakrabarti DP, Pilgrim A, Sastry MKS (2011) Wax formation in oil pipelines: A critical review. Int J Multiph Flow 37:671–694.

Andrade DEV, Cruz ACB, Franco AT, Negrão COR (2015) Influence of the initial cooling temperature on the gelation and yield stress of waxy crude oils. Rheol Acta 54:149–157.

Andrade DEV, Marcelino Neto MA, Negrão COR (2017a) The importance of supersaturation on determining the solid-liquid equilibrium temperature of waxy oils. Fuel 206:516–523.

Andrade DE V, Marcelino Neto MA, Negrão COR (2017b) Are the cooling rate, the crystals morphology and the yield stress directly related in waxy oils ? In: 24th ABCM International Congress of Mechanical Engineering. COBEM, Curitiba-BR, p 505

Davenport TC, Somper RSH (1971) The Yield Value and Breakdown of Crude Oil Gels. J Inst Pet 57:86–105.

El-Gamal IM (1998) Combined effects of shear and flow improvers: The optimum solution for handling waxy crudes below pour point. Colloids Surfaces A Physicochem Eng Asp 135:283–291.

Geri M, Venkatesan R, Sambath K, McKinley GH (2017) Thermokinematic memory and the thixotropic elasto-viscoplasticity of waxy crude oils. J Rheol 61:427–454.

Kané M, Djabourov M, Volle JL, et al (2003) Morphology of paraffin crystals in waxy crude oils cooled in quiescent conditions and under flow. Fuel 82:127–135.

Lee HS, Singh P, Thomason WH, Fogler HS (2008) Waxy oil gel breaking mechanisms: Adhesive versus cohesive failure. Energy & Fuels 22:480–487.

Lin M, Li C, Yang F, Ma Y (2011) Isothermal structure development of Qinghai waxy crude oil after static and dynamic cooling. J Pet Sci Eng 77:351–358.

Mullin JW (2001) Crystallization. 4th ed. Butterworth-Heinemann, London

Nývlt J, Hostomsky J, Giulietti M (2001) Crystallization (in portuguese). EdUFSCar/IPT, São Carlos - SP/BR.

Oliveira MCK, Teixeira A, Vieira LC, et al (2012) Flow assurance study for waxy crude oils. Energy & Fuels 26:2688–2695.

Pedersen KS, Rønningsen HP (2000) Effect of precipitated wax on viscosity - a model for predicting non-Newtonian viscosity of crude oils. Energy & Fuels 14:43–51.

Rønningsen HP, Bjorndal B, Hansen AB, Pedersen WB (1991) Wax precipitation from North Sea crude oils. 1. Crystallization and dissolution temperatures, and Newtonian and non-Newtonian flow properties. Energy & Fuels 5:895–908.

Sadeghazad A, Christiansen RL, Sobhi GA, Edalat M (2000) The prediction of cloud point temperature: In wax deposition. SPE J. doi: 10.2118/64519-MS

Singh P, Fogler HS, Nagarajan N (1999) Prediction of the wax content of the incipient wax-oil gel in a pipeline: An application of the controlled-stress rheometer. J Rheol 43:1437–1459.

Smith PB, Ramsden RMJ (1978) The prediction of oil gelation in submarine pipelines and the pressure requered for restarting flow. In: Europeans Offshore Petroleum Conference & Exhibition

Venkatesan R, Nagarajan NR, Paso K, et al (2005) The strength of paraffin gels formed under static and flow conditions. Chem Eng Sci 60:3587–3598.

Venkatesan R, Östlund JA, Chawla H, et al (2003) The effect of Asphaltenes on the Gelation of Waxy Oils. Energy & Fuels 17:1630–1640.

Wardhaugh LT, Boger D V. (1991) The measurement and description of the yielding behavior of waxy crude oil. J Rheol 35:1121–1156.

Webber RM (1999) Low temperature rheology of lubricating mineral oils: Effects of cooling rate and wax crystallization on flow properties of base oils. J Rheol 43:911–931.

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