



16th International Scientific Conference “Chemistry and Chemical Engineering in XXI century”
dedicated to Professor L.P. Kulyov, CCE 2015

The influence of processing conditions on the sedimentation kinetics of highly waxy crude oil

Y.V. Loskutova^a, N.S. Ryzhova^b, N.V. Yudina^a, E.V. Beshagina^{b*}

^aInstitute of Petroleum Chemistry Russian Academy of Sciences Siberian Branch, Akademichesky Avenue 4, 634021, Tomsk, Russian Federation

^bNational Research Tomsk Polytechnic University, Lenin av., 30, 634050, Tomsk, Russian Federation

Abstract

The research study of the effect caused by the temperature factor, additives, and magnetic field on the kinetics of sedimentation and pour point of high-paraffin low-resin oil demonstrated that treatment with the additives leads to decrease in oil sludge formation, variation of sedimentation rate and kinetics, however, joint effect of the additive and magnetic field provides no synergistic effect.

© 2015 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license

(<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Peer-review under responsibility of Tomsk Polytechnic University

Keywords: Asphaltene-resin-paraffin depositions, oil, pour point, “cold finger” method, additives.

1. Introduction

Asphaltene-resin-paraffin depositions (ARPD) precipitate, and they are sorbed on equipment surface under the effect of external factors during oil production and transportation. ARPD amount and composition is mainly determined by internal phase of oil and ambient conditions: temperature, pressure and fluid-flow effects¹⁻⁴. Commissioning of new oil and gas condensate fields in Western Siberia, Russia and, in particular, in Tomsk region, where oils are noted for relatively small amount of resin and asphaltene components as well as for high pour point due to elevated paraffin content, preconditions implementation of new arrangements and technologies providing uninterrupted oil production and transportation⁵⁻¹¹.

2. Testing procedures subjects and methods

* Corresponding author. Tel.: +7913-825-04-01.

E-mail address: reoloi@ipc.tsc.ru

Under standard conditions, the oil produced at Ondatrovoe field (Tomsk region, Russia) is a high-gravity ($\rho = 0.753 \text{ g/cm}^3$) and low-viscosity crude material containing no asphaltenes and about 1.5% wt of resins. It is characterized by its low bubble point (BP = 33 °C). However, due to elevated paraffin content (~ 6 % wt) the oil is noted for elevated pour point (minus 4.4 °C) and sharp growth of viscosity rating as temperature decreases to 0°C. Transportation and storage of such oil in wintertime requires use of specific methods improving its viscosity-temperature rating. Therefore, the scope of research study consisted in examination of effect caused by the temperature factor, comprehensive additives and magnetic treatment on oil sedimentation kinetics and pour point.

Kinetics of oil deposition formation was studied on a lab-scale plant based on the “cold finger” method simulating the process of paraffin sedimentation in the oil stream inside the oil pipeline. The plant consists of 4 steel rods (“fingers”) cooled down to 0 °C and placed into the examined 25 °C oil samples. The amount of depositions was gravimetrically determined under dynamic conditions at fixed time intervals during 1 hour as the average outcome of 2 simultaneous experiments ly. Oil sludge was extracted from the oil samples unaffected by heat treatment (NN oil) after 1 hour of cooling and thermostatic control at the temperature of 0 °C (NT oil)¹². The pour point depressants Difron 3004 (D04), Difron 3065 (D65), and Flexoil 1470 noted for their dispersing properties (concentration in oil is 0.05 % wt) and inhibiting formation of paraffins were used as additives. Magnetic treatment (MT) of NN oil was conducted at 25 °C under continuous flow conditions at the rate of 10 cm³/min using the lab-scale magnetic activator (induction is 0.3 - 0.4 T), the magnetic structure of which consists of 6 annular permanent magnets made of Nd – Fe – B alloy¹³.

3. Discussion of results

It was shown that treatment of both NN and NT oil with the additives reduces the amount of formed oil sludge (Fig. 1).

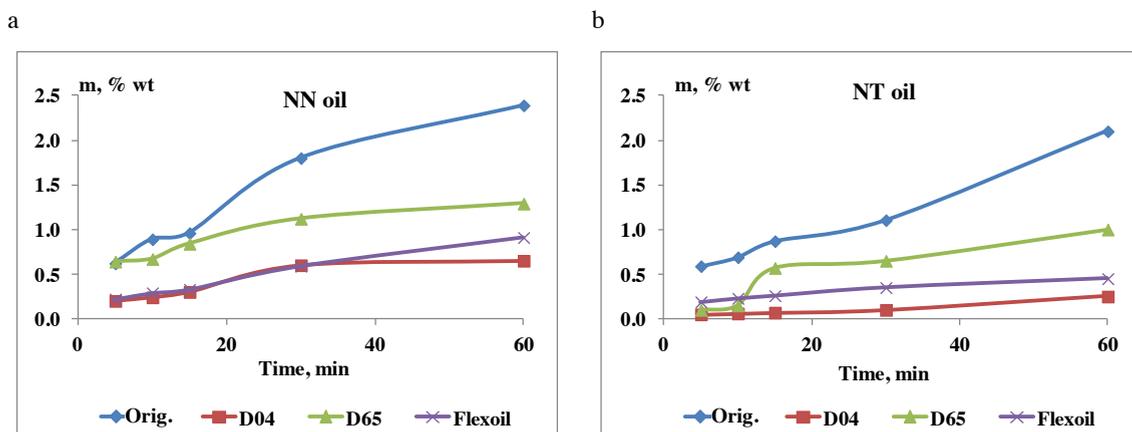


Fig. 1. (a) Time variation of oil sludge amount upon introduction of additives into NN and (b) (NT) oils

Regardless of temperature conditions, maximum decrease in oil sludge weight was observed upon introduction of Flexoil and D04 additives into 0.05% wt oil of Ondatrovoe field. Moreover, significant difference in sedimentation kinetics is observed between NN and NT oils treated with the additives. Thus, during the first 30 minutes, the amount of oil sludge formed in NN oil treated with Flexoil additive is equal to the one formed in the oil treated with D04 additive (Fig. 1 a). Subsequently, the efficiency of Flexoil additive decreases. During the first 10 minutes a negligible amount of oil sludge precipitates from NT oil treated with the additives. Further on, the efficiency of Flexoil additive slightly decreases, and the efficiency of D65 additive drops drastically. During the experiment, the sedimentation intensity is minimal for NT oil treated with D04 additive.

Sedimentation rate was calculated for various heat treatment conditions upon introduction of the additives (Fig. 2 a). As shown in the figure below, introduction of highly-efficient D04 additive into NN oil reduces the sedimentation rate by factor of 3.7 and is even more efficacious for NT oil by factor of 8.4, which amounts 80 g/m²*h.

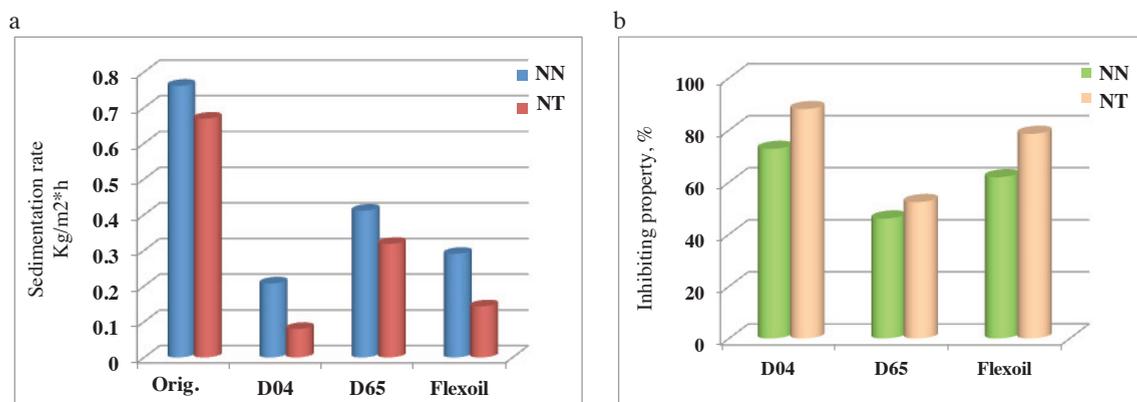


Fig. 2. (a) Sedimentation rate and (b) inhibiting property of additives for thermostatically controlled and non-thermostatically controlled oils

The thermostatic control mode to a great extent affects the inhibiting property of the additives under study, which block the sedimentation process. D04 additive is less dependent on temperature, and there is inverse relation between its efficiency and input temperature. The same is applicable to D65 additive.

Since all additives are chemical agents of comprehensive action, the impact of the additives on oil pour point was studied (Fig. 3 a). It was determined that only D04 additive makes it possible to reduce the NN oil pour point T_{pp} by 6.8 °C. When the oil is treated with other additives, T_{pp} variation is negligible and ranges within 2 to 3 °C regardless of thermostatic control mode.

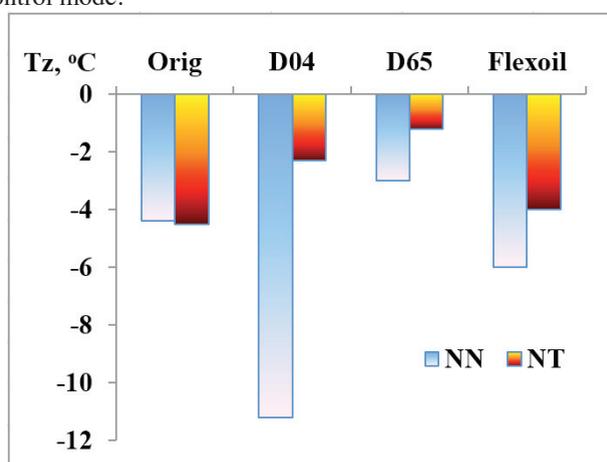


Fig. 3. Pour point of thermostatically controlled and non-thermostatically controlled oils upon introduction of additives

The option of comprehensive physicochemical oil treatment when exposed to magnetic field and introduction of the most efficient D04 additive was studied. During 10 minutes after magnetic treatment (MT), the ARPD amount drops only by 9% wp with further increase in treatment efficiency to 18% wp (Fig. 4 a).

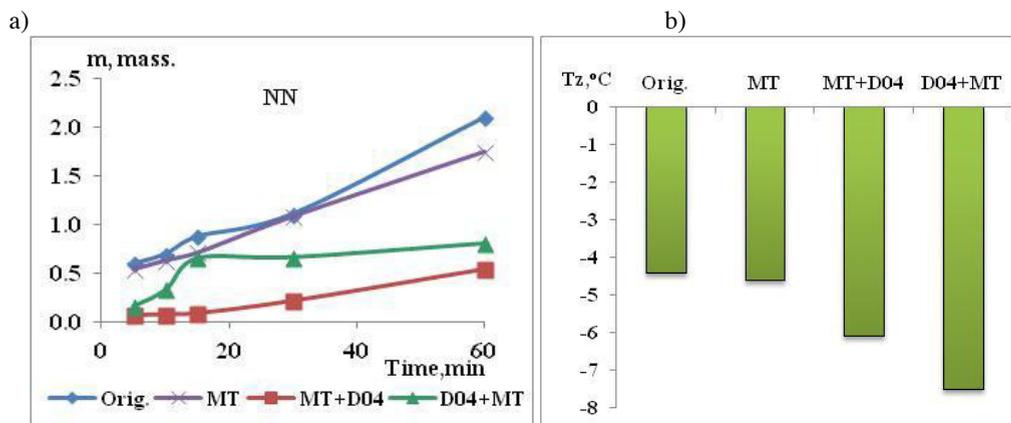


Fig. 4. (a) Time variation of oil sludge amount; (b) oil pour point after magnetic and physicochemical treatment

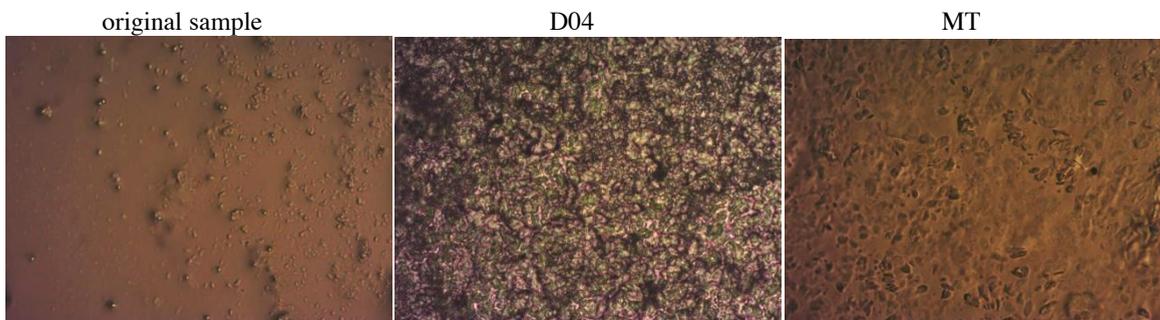
After introduction of D04 additive into magnetically treated oil, the effect of permanent magnetic field is almost leveled out during the first 15 minutes, and the intensity of paraffin deposits formation remains close to the one of the oil treated with the additive. Considerable growth of oil sludge amount is observed during the following hour. On the contrary, sedimentation dynamics of oil treated with the additive and subsequently exposed to magnetic treatment is close to sedimentation dynamics of oil exposed to magnetic field during 15 minutes. During the following 30 to 60 minutes ARPD formation intensity decreases.

The effect of magnetic field and physicochemical treatment on oil pour point was studied as well (Fig. 4 b). It was determined that during magnetic and combined oil treatment the negligible T_{pp} variation by 2 to 3 °C was observed.

It is common knowledge that inhibitive additives convert oil sludge into suspended form and retain highly-dispersed particles in the solution preventing coarsening and precipitation^{13,14}. Adsorption of additive on the dispersed particle surface prevents further consolidation of paraffins in the solution. Introduction of an additive at phase transition temperature during the initial stage of paraffins consolidation increases solubilizing property of the additive therefore stabilizing the colloidal system. Moreover, the effect of the additive consists in reduction of initial size of aggregates, stabilization thereof, and abatement of aggregation rate.

The exposure of oil to magnetic field leads to reorientation of the spins of paramagnetic fields, which, first of all, breaks the shell of complex base unit and entails alteration of rheological properties. During magnetic treatment of low-resin oils, major structure formation processes occur in supermolecular structure, they are characterized by destroying and/or formation of a new crystal lattice^{12, 15}.

Alteration of oil sludge structure is proven by the data obtained during microscopic observations (Fig. 5).



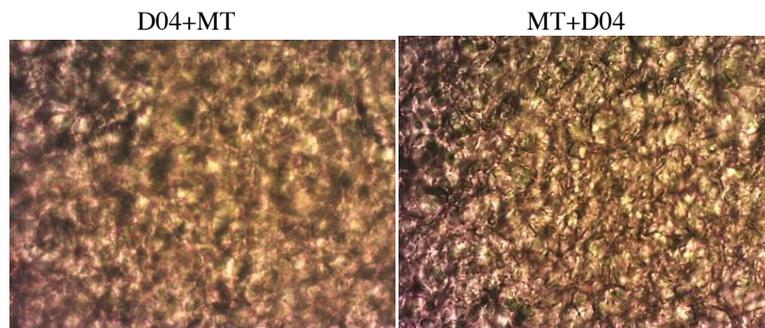


Fig.5. Photomicrographs of oil sludge extracted from oil 30 minutes after treatment

There are fine spheroidal particles in the structure of original oil sludge. 20 to 25 μm platelike paraffin aggregates are formed after D04 additive is introduced or magnetic treatment is performed. As the sampling period increases, the structure of oil sludge aggregates changes from clear dendritic platelike to combined dendritic-spherulitic. Increase in quantity and size of both spherical and dendritic crystalline particles is observed. After comprehensive treatment, the oil sludge maintains complex structure including spherical and platelike aggregates.

4. Conclusion

Following the results of conducted research study, it was demonstrated that treatment of both non-thermostatically controlled and cooled oil produced at Ondatrovoe field with the additives reduces the amount of formed oil sludge, alternates sedimentation kinetics and rate. Difron 3004 additive possesses ultimate inhibiting properties decreasing the amount of oil sludge by 88% upon introduction into oil cooled down to 0 °C causing, however, slight increase in pour point.

Combined oil treatment with magnetic field and additive provides no synergistic effect, i.e. no additional decrease in the amount of oil sludge or pour point was observed.

References

1. Mehrotra, A.K.; Bhat, N.V. *Energy & Fuels* 2010; 24:2240–2248.
2. Bidmus, H.O.; Mehrotra, A.K. *Ind. Eng. Chem. Res.* 2004; 43:791–803.
3. Mullakaev, M.S., Volkova, G.I., Gradov, O.M. *Theoretical Foundations of Chemical Engineering* 2015; 49:289–296.
4. Mullakaev, M., Asylbaev, D., Prachkin, V., Volkova, G. *Chemical and Petroleum Engineering* 2013; 9:11–13.
5. Pauly, J.P.; Daridon, J.L.; Coutinho, J.A. *Fluid Phase Equilib* 2004; 224:237–244.
6. Becker, J.R. *Oilfield paraffin treatments: Hot oil and hot water compared to crystal modifiers*; Proceedings of the 2000 Society of Petroleum Engineers (SPE) Annual Technical Conference and Exhibition (Production Operations and Engineering/General): Dallas, TX, Oct 1–4, 2000.
7. Bosch, F.G.; Schmitt, K.J.; Eastlund, B.J. *IEEE Trans. Ind. Appl.*; 1992.
8. Sarmiento, R. C.; Ribbe, G. A. S.; Azevedo, L. F. A. *Heat Transfer Eng.*; 2004.
9. Braden, B. *The use of enzymes to control paraffin and asphaltene deposits in the wellbore*. Proceedings of the Society of Petroleum Engineers (SPE) Western Regional Meeting; Long Beach, CA, June 25–27, 1997.
10. Ghedamu, M.; Watkinson, A. P.; Epstein, N. *Mitigation of wax buildup on cooled surfaces*. In *Fouling Mitigation of Industrial Heat-Exchange Equipment*; Panchal, C. B., Bott, T. R., Somerscales, E. F. C., Toyama, S., Eds. New York: Begel House, 1997.
11. Loskutova, Yu.V., Prozorova I.V., Yudina N.V., Rikkonen S.V. *Colloid Journal*; 2005:67:602–605.
12. Loskutova Yu.V. *Effect of Magnetic Fields on the Paramagnetic, Antioxidant, and Viscous Properties of Oils and Resin-Asphaltene Components*. In: Jeremy A. Duncan (Ed.), *Asphaltenes: Characterization, Properties and Applications*. Series: Chemical Engineering Methods and Technology. USA: Nova Science Publishers; 2010. p. 121-144.
13. Beshagina E.V., Yudina N.V., Loskutova Yu.V., Krutey A.A.. Paraffin Blockage Specifics in Model Petroliferous Systems. *Procedia Chemistry* 2014; 10:229–235.
14. Lopes-da-Silva J. A., Coutinho João A. P. Analysis of the Isothermal Structure Development in Waxy Crude Oils under Quiescent Conditions. *Energy & Fuels* 2007; 21:3612 – 3617.
15. Evdokimov I.N., Kornishin K.A. Apparent Disaggregation of Colloids in a Magnetically Treated Crude Oil. *Energy & Fuels* 2009:4016-4020.