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# Influence of Magnetic Field and Chemical Reagents on the Structural and Mechanical Properties of Paraffin Oil

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## Abstract

The effect of temperature factor, polymer additives and magnetic field on the kinetics of sediment formation, pour point and microstructure of oil residue from high-paraffin low-resin oil is investigated for the purpose of developing the methods aimed at a decrease in the rate of formation of asphaltene sediments during oil transportation and storage. Independently of the temperature conditions of action, the introduction of additives into oil causes a decrease in the amount of the formed sediments. The maximal inhibiting capacity is that of DP2 additive causing a decrease in the amount of oil sediments almost by a factor of 9. The combined treatment of oil with magnetic field and the additive does not lead to an additional decrease in the amount of the formed oil residue and pour point.

**Keywords:** high-paraffin oil, asphaltene-resin-paraffin sediments, polymer additive, magnetic processing, resin-asphaltene components

## INTRODUCTION

Permanently increasing demand for the production of energy carriers is currently observed all over the world. To meet this demand, oil companies have to develop the deposits of heavy oil under unfavourable conditions in hard-to-reach regions. In this situation, transportation of highly viscous and highly chilling paraffin oil along pipelines is a critical problem for oil producing industry.

Production and transportation of paraffin oil under the conditions of low environmental temperature involve the formation of asphaltene-resin-paraffin sediments (ARPS) on the surface of exhaust lines and tubes, till complete plugging [1]. An increase in oil viscosity and the roughness of the equipment wall surface, accumulation of sediments in technological and storage reservoirs cause failures of the equipment, interferes with the operation of valves and measuring devices. All these factors may finally result in a decrease in productivity, suspension of production and an increase in the expenses for pumping over. Oil transportation along pipelines becomes a highly energy-consuming process. In the world practice, economic losses from ARPS are estimated as several million dollars every year: usual capital repairs of a well costs about 250 thousand US dollars [2]. Therefore, a control over ARPS formation is of prime importance.

It is known that petroleum residue is a combination of paraffin hydrocarbons of the $C_{16}$–$C_{70}$ series with resin and asphaltene components (RAC). Under the normal bed conditions, paraffin hydrocarbons are in equilibrium with other oil components, but their deposition starts with a decrease in temperature to a point called cloud point or the temperature of phase transition. The major factors affecting the changes in the equilibrium in oil and leading to the deposition of oil sediments are changes in pressure, evaporation and the loss of dissolved gases [3–6]. The mechanisms of ARPS deposition include molecular diffusion, thermal diffusion (Soret effect), Brownian diffusion, mechanisms of gravitational scattering and dispersion of coagulated particles in the shear field, and deposition in a two-phase flow. Deep understanding of deposition mechanism and decisive factors is necessary for a control over the process of ARPS formation.

The main methods against ARPS include mechanical and chemical methods, the major problem of which is in high requirements to ecological safety. The method involving the action of magnetostatic field is widely used in various branches of industry to purify waste waters, feedwater in boiler installations, inorganic sludge and emulsions, and to enhance the efficiency of fuel combustion [7–9].

At present, some manufacturers including Russian ones have passed to the mass production of various magnetic devices providing activation of liquid media to meet the needs of oil industry [10–13]. However, it is difficult to find readily available information on the results of successful field tests of magnetic devices in improving the viscosity and temperature characteristics of oil and a decrease in ARPS. As a consequence, large oil companies are reluctant in introducing magnetic technologies at mines [14, 15].

In parallel with industrial introduction of magnetic devices, laboratory studies are carried out to reveal the features of behaviour of oil-containing systems in the magnetic field [16–21]. In spite of a permanent increase in the amount of these studies, there is a lack of reliable data describing a connection of phase transformations of RAC and paraffin hydrocarbons with the structural-rheological characteristics of oil after magnetic treatment (MT). In addition, suitable mathematical models that could explain the effect of magnetic field on complicated oil-containing objects are absent. A large number of parameters affecting the formation of ARPS bring complications into choosing such a model [22].

Implementation of any new technology requires high expenses, so it appears more efficient and reasonable to use MT in combination with other traditional methods, such as chemical treatment, thermal treatment etc.

The goal of the present work is investigation of the effect of temperature factor, polymer additives and magnetic field on the kinetics of deposition, chilling temperature and microstructure of oil sediments from high-paraffin low-resin oil.

## EXPERIMENTAL

The object of investigation was oil from the Ondatrovoe deposit (the Tomsk Region). Under standard conditions, it is characterized as light ($\rho = 0.753$ g/cm$^3$), low-viscous, with the low temperature of initial boiling ($T_b$ = 33 °C). This oil does not contain asphaltenes; resin content is about 1.5 mass %. However, due to an increased content of solid high-molecular paraffins (6 mass %), a sharp worsening of the structural-mechanical properties of oil occurs at the environmental temperature below 5 °C: viscosity and the limiting shear strain increase, and a substantial amount of oil precipitate is formed.

The quantitative evaluation of precipitation process by means of the cold finger was carried out in a laboratory set-up modelling the formation of oil precipitate [23–25]. The set-up consisted of four steel rods cooled to 0 °C, which were placed in hermetic beakers with oil samples under analysis at a temperature of 25 °C. The formation of the precipitate on a rod occurs due to temperature gradient under permanent mixing and thermostating. The amount of the precipitate ($m$) was determined using he gravimetric method within 60 min in fixed time intervals as an average value from two parallel experiments. The precipitates were obtained from two oil samples: initial (in) – without thermal treatment, and cooled (cool) – after cooling and thermostating for 60 min at 0 °C.

Oil treatment was carried out using commercial additives Diffron 3065 (DP1) and Diffron 3004 (DP2) (LC Kompaniya Toplivnyi Region, Russia) and Flexoil WR1740 (DP3) (Champion Technologies Russia & Caspian BV), possessing depressing, dispersing and inhibiting properties with respect t paraffin formation. According to the data of developers, the polymer basis of the additives is represented by poly(alkyl)acrylates and poly(alkyl)metacrylates with different molecular masses. The additives were introduced in the working concentration of 0.05 mass % under continuous mixing during 5 min (into initial oil – at room temperature, into cooled oil – at 0 °C).

Magnetic treatment of oil was carried out with the help of a magnetic system (MS) composed of a flow-type magnetic activator MAUT (LC PKF Eksi-Key, Tomsk, Russia). This magnetic system includes composite magnetically hard materials based on the alloys of rare earth metals Nd–Fe–B. The amplitude of magnetic induction at the inner pole concentrators was up to 0.6 T, and at the outer ones it was up to 0.4 T (Fig. 1). The

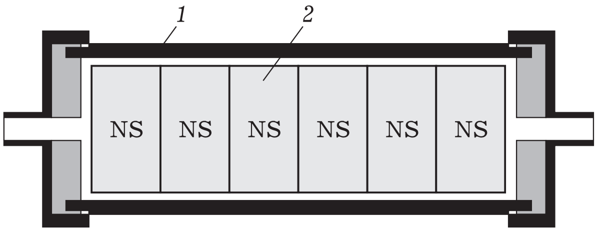


Fig. 1. Scheme of MAUT device: *1* – housing, *2* – magnetic system.

effect of magnetic field on the viscosity and temperature was studied in the flow mode. During laboratory experiments, oil under investigation was passed along a Teflon tube 3.5 mm in diameter through the MS at 20 °C with the flow rate of 10 $cm^3$/min.

Determination of oil chilling temperature ($T_{ch}$) before and after different kinds of action was carried out using an INPN Kristall SX-800 instrument (Russia, No. 31553-06 of the State Registry of RF) with the measurement error of ±2 °C. Difference between the results of two measurements of $T_{ch}$ did not exceed 1 °C.

## RESULTS AND DISCUSSION

For initial and cooled oil samples, investigation of the effect of DP1, DP2 and DP3 additives on the dynamics of oil precipitate formation was carried out. It was demonstrated that treatment with the additives causes a decrease in the amount of precipitate with time (Fig. 2). The maximal decrease in the mass of the precipitate (by 88–91 %), independently of the temperature regime of oil preparation, is observed after the addition of DP2 and DP3. The dynamics of precipitation in the presence of the additives is different for initial and cooled oil. For instance, the amount of precipitate formed in the sample of initial oil treated with DP2 additive is the same as that formed in oil with DP3 additive during the first half of the experiment (see Fig. 2, *a*). After that, the efficiency of DP3 starts to decrease.

Cooled oil treated with additives forms a substantially smaller amount of oil precipitate on the metal rod during the first 10 minutes of the experiment than non-cooled oil does (see Fig. 2, *b*). Then the efficiency of DP3 additive starts to decrease slightly, while the efficiency of DP1 drops down sharply. The DP2 additive conserved efficiency in preventing precipitation during the entire experiment (60 min).

Additives used in the work are the reagents of integrated action, so we studied their effect on oil chilling temperature (Fig. 3). It was established that the addition of DP2 into initial oil allows a decrease in $T_{ch}$ by 6.8 °C (see Fig. 3, *a*). Insignificant changes in $T_{ch}$ by 2–3 °C are observed after oil treatment with other additives, independently of thermostating mode.

The effect of the integrated action of magnetic field and the most efficient additive DP2 on oil samples under investigation was also studied. Integrated treatment, which involved the magnetic action on initial oil sample and subsequent introduction of DP2 additive in the amount of 0.05 mass %, was designated as MT+DP2, while the treatment in the magnetic field after the introduction of the additive was designated as DP2+MT. It was established that $T_{ch}$ changes only slightly – by 2–3 °C, independently of treatment sequence (see Fig. 3, *b*).

The kinetic dependences (for 60 min) of the formation of oil precipitate after different kinds of physicochemical action are shown in Fig. 4. In

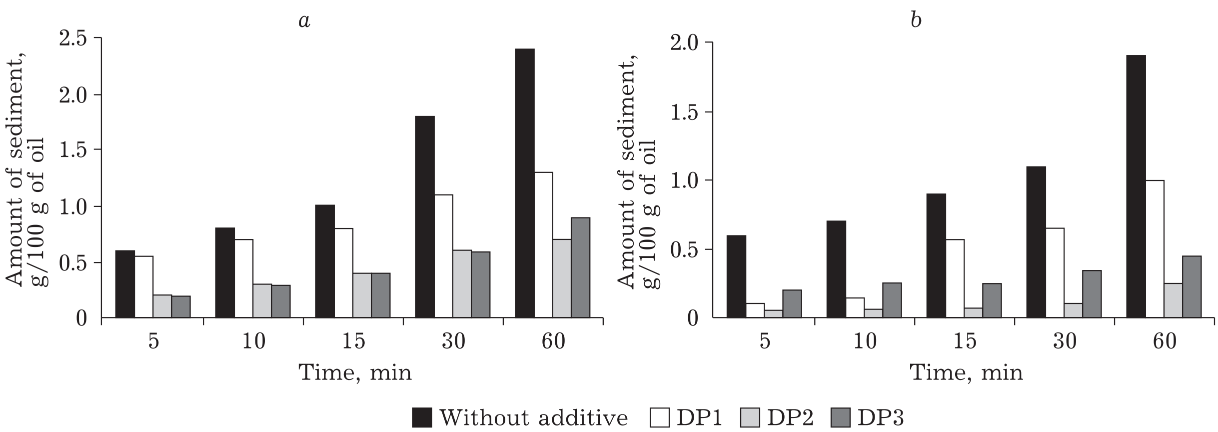


Fig. 2. Effect of DP1, DP2 and DP3 additives on the kinetics of precipitation in initial oil (*a*) and in oil cooled to 0 °C (*b*).

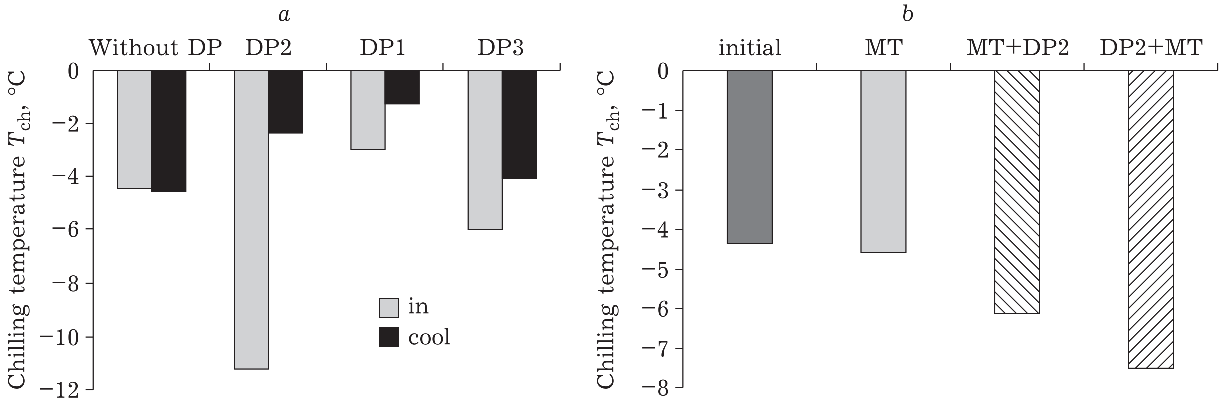


Fig. 3. Comparison between chilling temperatures of non-thermostated (in), thermostated (cool) oil with DP1, DP2 and DP3 additives (*a*) and oil samples after magnetic treatment (MT) and integrated treatment (*b*).

10 min after MT, the amount of the precipitate decreases by 9 %, but by the end of experiment – by 18 % (see Fig. 4, curve *2*). It is possible that cyclic treatment involving 2-3 cycles is to be used to increase the efficiency of MT.

The highest efficiency in preventing precipitation was demonstrated by the complex additive DP2 (see Fig. 4, curve *3*). During the first 15–20 min, a minimal amount of precipitate is formed, later the intensity of precipitation increases but much lower than after MT.

The amount of the formed precipitate after integrated treatment DP2+MT (see Fig. 4, curve *4*) increases substantially during the first 15 min. Then, till the end f experiment, the intensity of ARPS formation changes insignificantly.

It is known that additives inhibiting precipitation in oil transform oil sediments into suspended state and hold fine particles in solution preventing their agglomeration and sedimentation [26–28]. Adsorption of the additive on the surface of a disperse particle prevents subsequent aggregation of paraffins in solution. The introduction of the additive at the initial stage of paraffin aggregation at a temperature close to the point of phase transition enhances its solubilising ability and stabilises the colloid system. The effect of the additive is in decreasing the initial size of aggregates, their stabilization and a decrease in the rate of aggregation.

The application of magnetic field on the oil system leads to the destruction of the existing structure due to the rupture of bonding between the weak dipoles of paraffins (*n*-alkanes with chain length $>C_{16}$) and the formation of additional reaction centres in resinous-asphaltene components. Under the action of the magnetic field on the oil system, high activity is exhibited by asphaltenes and resins possessing paramagnetic and diamagnetic properties; they play the part of a structural mechanical barrier on the crystal surface of paraffins thus increasing the depth and rate of their destruction. Resin-asphaltene components block the formation of highly porous rigid gel-like structure formed by a three-dimensional network of interconnected paraffin crystals [21, 29].

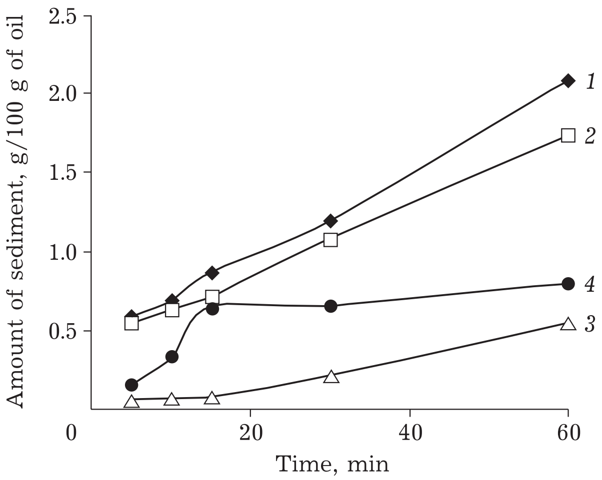


Fig. 4. Kinetics of the formation of precipitate in oil: *1* – initial, *2* – after magnetic treatment (MT), *3* – after integrated treatment MT+DP2, *4* – after integrated treatment DP2+MO.

The data of optical microscopy confirm the conclusions concerning the changes in the structure of oil precipitate (Fig. 5). After MT, the formation of aggregates with plate structure 20–25 μm in size takes place. With an increase in the period of sampling, a transition of clearly pronounced plate-dendrite structure into a mixed dendrite-spherulite one occurs. This is accompanied by an increase in the number of size of crystallites, both with spherical and dendrite shape. After integrated treat-

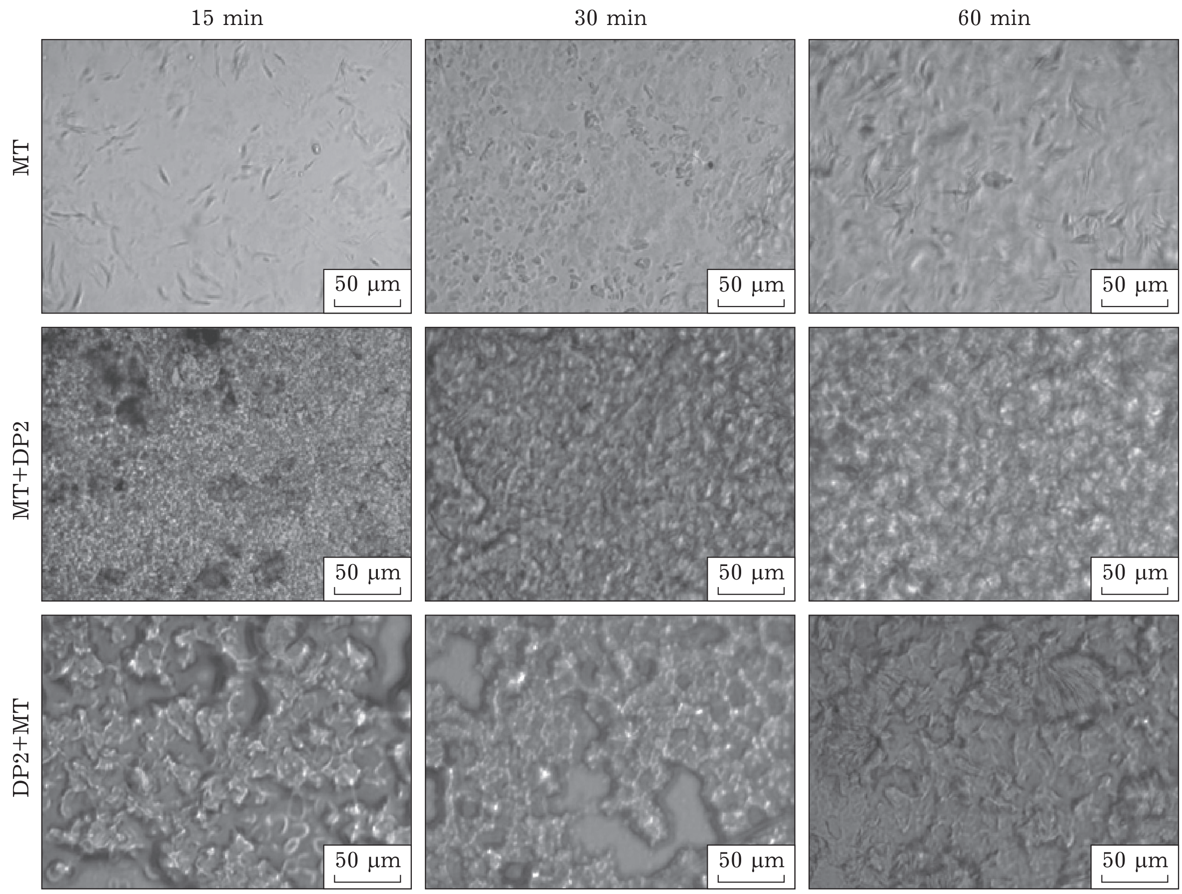


Fig. 5. Microphotograph of sediments isolated from oil in 15, 30 and 60 min after different kinds of treatment.

ment (MT+DP2 and DP2+MT), the precipitates have complicated structure, too; they contain coarse spherical and plate-like aggregates.

### CONCLUSION

Treatment of high-paraffin low-resin oil from the Ondatrovoe deposit by the additives of complex action, either under standard conditions or after cooling to a temperature close to the chilling point, causes a decrease in the amount of the formed oil precipitate and a change in the dynamics of precipitation.

The maximal inhibiting capacity was demonstrated by the additive based on poly(alkyl)acrylate and poly(alkyl)metacrylate of Diffron 3004 grade (DP2), which causes a decrease in the amount of sediments in oil by 88 % and chilling temperature by 6.8 °C. The action of magnetic field has diverse effects on the amount of oil residue, the kinetics of precipitation, and is accompanied by complete or partial destruction of the crystal structure of oil paraffin. The integrated treatment of oil with the magnetic field and the additive does not lead to the expected synergism and does not result in any additional decrease in the amount of oil precipitate and chilling temperature.

The low efficiency of the combined treatment may be connected with the absence of asphaltenes in oil and with the presence of a small amount of resins, these components being responsible for the formation of new reactive centres that are able to alter the existing structure and hence to affect the viscosity and temperature related parameters.

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