Journal of Engineering Physics and Thermophysics, Vol. 76, No. 3, 2003

INDUSTRIAL SYNTHESIS AND EVALUATION OF THE HYDRODYNAMIC EFFICIENCY OF POTENTIAL AGENTS FOR DECREASING RESISTANCE IN PETROLEUM PIPELINES

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UDC 66.091:665.7.035.6:532.517.4

The influence of anti-turbulence additives on the decrease in the hydrodynamic resistance in main pipelines is investigated. The dependence of the Thoms effect on the physicochemical properties of a polymer obtained on an industrial plant is analyzed. The method for evaluating the efficiency of potential agents of decreasing the hydrodynamic resistance is proposed.

To increase the carrying capacity of petroleum pipelines and to decrease the expenditure of energy on transporting a unit liquid volume one usually uses the traditional methods of decreasing viscosity: heating, dilution with a low-viscosity solvent, and introduction of depressant additives. The above-listed methods are efficient for the laminar regime of flow, in which the volumetric rate of flow of the liquid is inversely related to its viscosity. But in the overwhelming majority of cases, in the process of transport of petroleum and petroleum products in pipelines, there takes place a turbulent regime of flow in which the volumetric rate of flow of the liquid is weakly dependent on the viscosity. For example, in the laminar regime of flow, a twofold decrease in the viscosity causes a twofold increase in the mean rate of flow as well, while in the turbulent regime the same decrease in viscosity leads to an increase of only 10% in the rate.

Because of this, energy-conserving technologies of pipeline transport with the use of anti-turbulence additives, which, without changing the viscosity, partially laminarize the flow and thus decrease the dissipative energy loss, have been used with increasing frequency in recent years.

In the literature reviews [1, 2] devoted to the Thoms effect, the hydrodynamic properties of tens of anti-turbulence additives efficient under laboratory conditions have been described. But not all of these additives, on being introduced into industrial pipelines, were able to decrease the resistance. This disparity is explained by the fact that in the majority of cases, researchers studying the behavior of polymeric solutions sought to model flows with Reynolds numbers identical to those in active pipelines on laboratory stands and overlooked, in so doing, the shear stress on the pipe wall τ_w. These important hydrodynamic parameters of turbulent flow are related to the pipe diameter D, density ρ, and kinematic viscosity ν of the liquid by the functional relation

$$\mathrm{Re} = 6.32\,(\tau_w/\rho)^{0.57}\,(D/\nu)^{1.14}\,. \tag{1}$$

It follows from Eq. (1) that to provide flow of a liquid with fixed viscosity and density at a given Re = const in laboratory-plant pipes of small diameter, it is necessary to apply much higher shear stresses (several orders of magnitude higher) than those in the main pipelines to attain the same value of the Reynolds number. For example [3], in the Aleksandrovskoe–Anzhero-Sudzhensk pipeline with a diameter of 1.2 m, petroleum with a kinematic viscosity of $5\cdot10^{-6}$ m^2/sec and a density of 850 kg/m^3 is transported at a shear stress of 3 Pa, which corresponds to the turbulent regime with Re = $3.5\cdot10^5$. To provide petroleum flow with the same Reynolds number in a turbulent flow meter with a pipe diameter of $2\cdot10^{-3}$ m it is necessary to apply $\tau_w = 1\cdot10^6$ Pa, which is six orders of magnitude higher than that in the above-mentioned pipeline. But first, such shear stresses are difficult to realize under laboratory conditions, since

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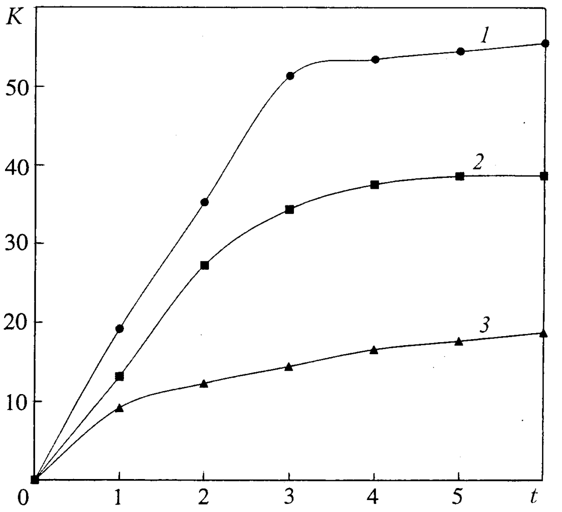


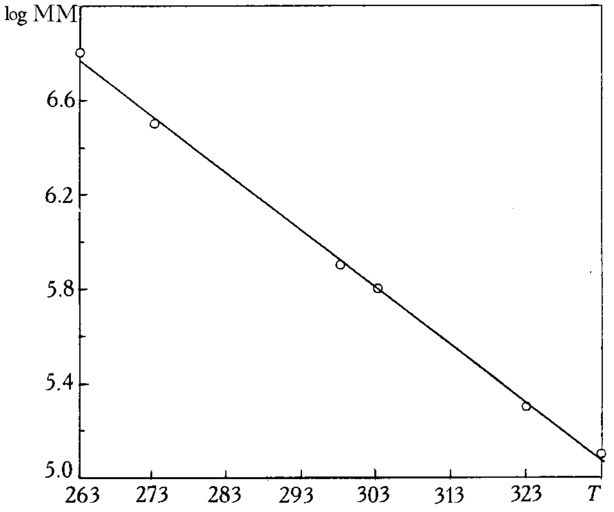


Fig. 1. Dependence of the conversion of different monomers on the polymerization time: 1) hexene-1, 2) octene-1, and 3) decene-1. t, h; K, wt.%.

Fig. 2. Dependence of the logarithm of the molecular mass on the polymerization temperature. T, K.

to do this it is necessary to provide a pressure drop of $\Delta p = 2 \cdot 10^3$ kg/cm^2 in the 1-m-long pipe of the laboratory flow meter. Second, it has been experimentally established that at fairly high shear stresses, even oligomers begin to show the capacity for decreasing resistance.

Because of this, considering the existence of turbulence (Re > 2300) to be a necessary condition for the Thoms effect, we nonetheless believe that the value of the Reynolds number is of secondary importance while the value of the shear stress on the pipe wall, which in laboratory experiments should be no higher than that in the main pipelines, is of primary importance. This approach is theoretically substantiated by the equation relating the increment in the volumetric flow rate to the hydrodynamic parameters of flow and the physicochemical characteristics of solutions [4]:

$$\Delta Q = S\psi\tau_w \left[1 - (G/\tau_w)^{1/2}\right]/(\rho G)^{1/2} , \qquad (2)$$

where $\Delta Q = Q_p - Q_s$ is the increment in the volumetric rate of flow of a polymeric solution Q_p as compared to the volumetric rate of flow of a pure solvent Q_s at equal shear stresses $\tau_w = \Delta p R_w / 2L$ on the pipe wall, $S = \pi R_w^2$, $\Psi = [\eta]C/(1 + [\eta]C)$, and $G = RT/([\eta]M)$.

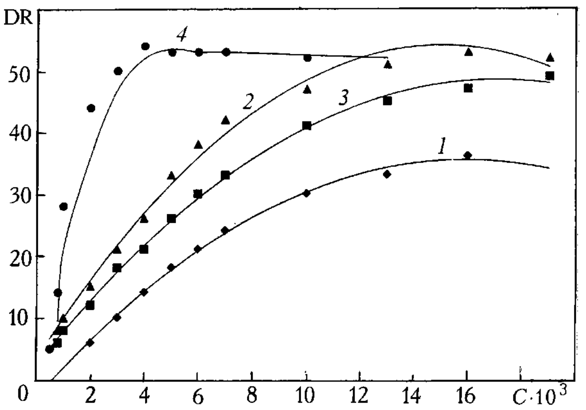
It follows from Eq. (2) that the Thoms effect ($\Delta Q > 0$) appears at a positive value of the algebraic sum in brackets, i.e., when the condition $[1 - (RT/([\eta]\, M\tau_w))^{1/2}] > 0$ is fulfilled or

$$[\eta]\, M\tau_w/(RT) > 1 . \qquad (3)$$

Having equated the left-hand side of inequality (3) to unity, we can calculate the "threshold" shear stress $\tau_{thr} = RT/([\eta]M)$, i.e., the minimum stress beginning with which the velocity of turbulent flow of the polymeric solution begins to be higher than the velocity of flow of the pure solvent.

Analysis of (3) shows that the lower the shear stress, the higher the characteristic viscosity and the molecular mass, and the lower the temperature, the more hydraulically efficient is the polymeric sample. In industrial petroleum-product pipelines, τ_w has, as a rule, low values in the range from 1 to 10 Pa; therefore, polymers with a superhigh molecular mass ($M > 10^3$ kg/mole) and a high characteristic viscosity ($[\eta] > 1$ m^3/kg) are efficient. Thus, if M and $[\eta]$ of the polymeric sample, the temperature of the solution, and the shear stress on the wall of a concrete pipeline are known and (3) is fulfilled, a positive result from the application of a polymeric additive can be predicted theoretically.

It follows from inequality (3) that the efficiency of an additive depends not only on the molecular mass of the sample, but also on the quantity $[\eta]$ that characterizes the thermodynamic compatibility of the polymer with the



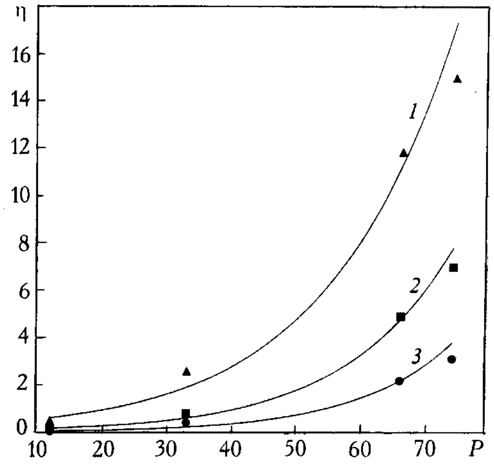


Fig. 3. Concentration dependence of the effect of decreasing the resistance of polyhexene-1 samples obtained at different initial concentrations of the monomer: 1) 10, 2) 15 (t = 8 h, K = 27%), 3) 15 (t = 24 h, K = 58%), and 4) 20 vol.%. C, kg/m^3; DR, %.

Fig. 4. Dependence of the dynamic viscosity of the reaction mass of polyhexene on the concentration at different rates of shear: 1) γ = 5.4, 2) 16.2, and 3) 48.6 sec^{-1}. P, kg/m^3; η, Pa·sec.

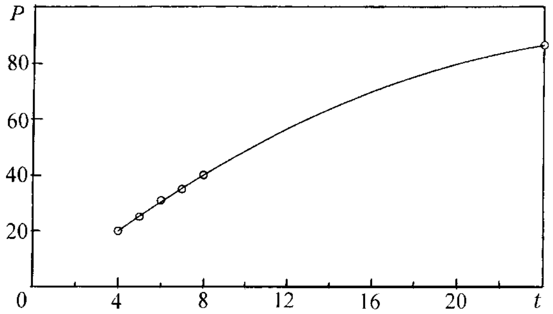
solvent. Petroleum is a multicomponent system whose properties are determined by the relative content of saturated, cyclic, and aromatic hydrocarbons in it as well as by the presence of polar components containing heteroatoms in their structure. Of the series of the investigated polymers of different chemical nature (polystyrene, polyacrylates, polyisoprene, polybutadiene, and others), universal compatibility with petroleum and petroleum products is exhibited by x-ray amorphous poly-α-olefins: polyhexene, polyoctene, and polydecene. They, being synthesized in a heptane solution by the ion-coordination mechanism in the presence of Ziegler–Natta catalysts (macrospherical titanium trichloride and diethylaluminum chloride), have a superhigh molecular mass ($MM > 1 \cdot 10^6$).

In the process of polymerization of hexene-1, octene-1, and decene-1 under laboratory conditions, it has been established that hexene-1 possesses the maximum activity and, consequently, the maximum rate of transformation into polymer (Fig. 1); therefore, it is precisely this monomer that was preferred in industrial production of the polymer.

It is known [5] that the molecular mass of polyolefins depends on the temperature of synthesis and the concentration of the monomer. The laboratory syntheses carried out by us [6] have shown (Fig. 2) that the polymeric samples with a molecular mass of several million can be obtained at a temperature lower than 10^{o}C. The numerical values of the characteristic viscosity of samples synthesized in this temperature range are in the region of 1 m^3/kg; therefore, the industrial production of polyhexene batches in the reactor was carried out at zero temperature, which assured the output of the product with fairly high values of $M > 10^3$ kg/mole and $[\eta] > 1$ m^3/kg.

The value of the molecular mass of the synthesized polymer and, consequently, its hydrodynamic efficiency depend not only on the initial concentration of the monomer in the reaction mixture, but also on the time of synthesis (Fig. 3). As is seen from the figure (curves 2 and 3), the efficiency of the polymer decreases with increase in the time of synthesis (8 and 24 h, respectively) and the depth of conversion from 27 to 58%. This drop in the effect is explained by the accumulation of low-molecular-weight "ballast" fractions in the polymeric solution, which are formed at the final stages of polymerization when the reaction mixture is already depleted of the monomer. But the low-molecular-weight "tails" not only decrease the efficiency of the anti-turbulence additive but, in the case of deep conversion, also sharply increase the viscosity of the concentrate (Fig. 4), which hampers its removal from the reactor and batching into the main petroleum pipeline. Because of this, the polymerization of polyhexene was terminated when an ~30% conversion was attained.

The industrial synthesis of polyhexene was carried out in an R301 batch reactor equipped with an anchor agitator. The volume of the reactor was 3 m^3 and of the reaction mixture 2 m^3. Batching was carried out in the following order: we poured the solvent (heptane), the monomer in an amount of 15% of the solvent, and a cocatalyst



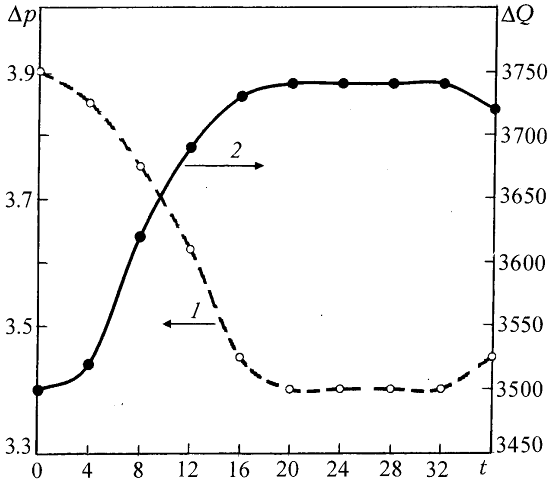


Fig. 5. Dependence of the polyhexene content in the concentrate on the polymerization time in the reactor. *t*, h; *P*, kg/m^2.

Fig. 6. Change in the volumetric rate (1) and the pressure drop (2) in the section of the Tikhoretsk–Novorossiisk pipeline with time in the case of pumping of a polymeric additive. *t*, h; Δ*p*, MPa; Δ*Q*, m^3/h.

solution and blew the mixture with nitrogen to remove oxygen. The mixture was simultaneously cooled. When a temperature of 0^oC was attained, we introduced a suspension of the catalyst in heptane. The conversion of the monomer was controlled gravimetrically by the fixed residue. The change in the content of the polymer in the solution with time, presented in Fig. 5, is described by the correlation equation $P = -0.1033t^2 + 6.2425t - 3.2259$. The polymerization was carried out for 8 h, whereupon the polymer solution was removed to a special container where a nitrogen pillow was formed above the product.

Rapid analysis of the hydrodynamic efficiency of the polymer batches obtained was made on a turbulent flow meter [7] at the shear stress $\tau_{lab} = 4$ Pa and $Re \geq 5000$. The effect of decreasing resistance was calculated from the formula

$$DR = [(\lambda_s - \lambda_p)/\lambda_s]\cdot 100\% . \tag{4}$$

For the solvent we used gasoline, which is analogous to petroleum in dissolving ability, but, being a low-viscosity liquid, makes it possible to test polyhexene in the turbulent region of flow when the very important condition

$$\tau_{thr} < \tau_{lad} \leq \tau_{pipe} \tag{5}$$

is fulfilled. It follows from (5) that laboratory testing of polymeric additives must be carried out at shear stresses no higher than the actual shear stresses existing in concrete pipelines τ_{pipe}, in which agents of decreasing resistance will be used.

The polyhexene batch produced by the method described at the Tomsk Petrochemical Plant was tested on the Tikhoretsk–Novorossiisk pipeline, in which a turbulent regime of flow ($Re = 5\cdot 10^4$) is realized at the shear stress $\tau_{pipe} = 6$ Pa and a volumetric rate of flow of 3500 m^3/h. Batching of the polymeric solution into the section of a pipe of diameter 0.8 m and length 125 km was carried out for 32 h, and a concentration of 8 g/m^3 of the polymer in petroleum was maintained. As the pipe was filled with petroleum with a polymeric additive, the friction loss of pressure decreased and the volumetric rate of flow simultaneously increased (Fig. 6, curves 1 and 2). The effect of decreasing resistance (22%) attained in this case is comparable with the effect (21%) [3] attained earlier on the Aleksandrovskoe–Anzhero-Sudzhensk pipeline into which the polymer was introduced in an amount of 40 g/m^3. The use of the polymer produced by the optimized technology of synthesis of high-molecular-weight poly-α-olefins made it possible to attain the same effect at a five times lower concentration.

NOTATION

Re, Reynolds number; τ_w, shear stress, Pa; ρ, density of the liquid, kg/m^3; D, diameter of the pipeline, m; ν, kinematic viscosity of the liquid, m^2/sec; Δp, pressure drop in the pipeline section, Pa; Q, volumetric rate of flow, m^3/sec; R_w, radius of the pipeline, m; L, length of the pipeline, m; S, cross-sectional area of the pipe, m^2; Ψ, volume fraction of polymeric coils in the solution; C, concentration of the diluted polymeric solution in the pipeline, kg/m^3; $[\eta]$, characteristic viscosity of the polymeric solution, m^3/kg; G, modulus of elasticity of macromolecular coils, Pa; M, molar mass of the polymer, kg/mole; R, universal gas constant, J/(mole·K); T, absolute temperature, K; MM, molecular mass of the polymer; DR, effect of decreasing the hydrodynamic resistance, %; λ, coefficient of hydrodynamic resistance; η, dynamic viscosity of the liquid, Pa·sec; K, conversion, %; t, time of synthesis, h; P, content of polyhexene in the reaction mixture, kg/m^3; γ, rate of shear, sec^{-1}. Subscripts: w, wall; thr, threshold; lab, laboratory; pipe, in the pipeline; p, polymeric solution; s, pure solvent.

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