comparison, we show in Fig. 2b the velocity distribution for turbulent flow (Re_d = 5400) at a distance of 100 mm from the inlet to the channel for various PAA concentrations.

It can be seen from Fig. 2 that on the initial segment a velocity profile is formed. The velocity distribution depends substantially both on the cross section selected and on the regime of flow of the polymer solution. The added polymer substantially affects the kinematic characteristics of the flow. As the solution becomes more concentrated, the velocity field is deformed. In the case of laminar flow the velocity diagram becomes elongated along the stream and becomes less full. Analyzing the nature of the deformation of the velocity field, we can assume that the velocity diagram for water with polymer additives on the initial segment of a rectangular channel resembles the velocity diagram on the uniform-flow segment, i.e., the initial or accelerated segment is reduced.

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TRANSIENT AND STEADY-STATE RHEOLOGICAL BEHAVIOR IN STRUCTURED HYDROCARBON SYSTEMS

I. G. Bulina, O. A. Karaev,
F. A. Kougiya, and A. G. Golubkov

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Crude paraffin-rich petroleum has been used to examine the structural changes in non-Newtonian hydrocarbon systems in steady-state and transient modes of flow, which include various relaxation processes.

The rheological behavior of crude petroleum is of some considerable interest [1-5], particularly since oil rich in paraffin hydrocarbons constitutes an increasing proportion of oil output, which gives considerable interest to the structural changes occurring under strain. Crude oil of this type constitutes a structured two-phase system with coagulation features, so one needs to know the laws governing the thixotropic behavior of the structure under shear.

The various phenomena involved in the disruption of the structure and the recovery have not been examined in detail, especially for alkane-rich petroleum in transient states of deformation and also at low shear rates (around 10^{-3} sec^{-1}), where the structural changes are the most pronounced.

Here we present results on the rheological features of two types of oil from the Mangyshlak deposit differing in alkane levels, and the data provide some additional information on these points.

We used a Weissenberg rheogoniometer of cone–plane type of diameter 5 cm and cone angle 2° in the working part. The results were processed in the normal way for this method [6]; the measurements were made at 20°C.

The structural changes may be deduced from three types of data: flow curves, stress-variation curves during strain, and stress relaxation after strain. We were able to relate the data from such curves to features of the structure.

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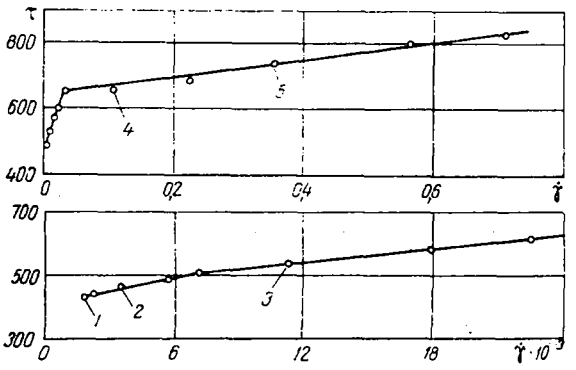

Fig. 1. Flow curves for Zhetybai petroleum (T = 20°C); the numbers on the curves are in accordance with the data given in Fig. 2a and Fig. 3.

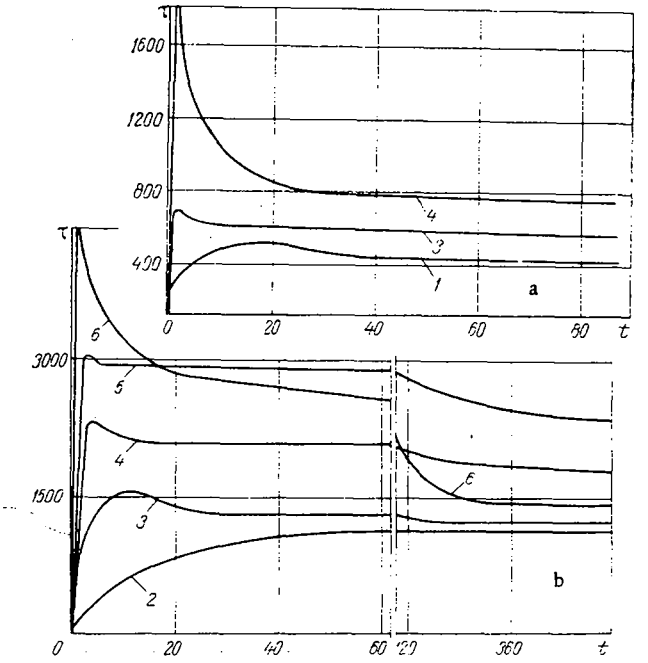

Fig. 2. a) Time course of tangential stress in Zhetybai petroleum at 20°C for shear rates (sec^{-1}) of: 1) $1.42 \cdot 10^{-3}$; 3) $1.12 \cdot 10^{-2}$; 4) $1.12 \cdot 10^{-1}$; b) corresponding curves for Uzen petreleum at 20°C for shear rates (sec^{-1}) of: 2) $3.55 \cdot 10^{-3}$; 3) $1.12 \cdot 10^{-2}$; 4) $3.55 \cdot 10^{-2}$; 5) $1.12 \cdot 10^{-1}$; 6) 1.12. Time t in sec; τ in dyn/cm^2.

Figures 1-3 show these data for petroleum from the Zhetybai deposit; Figs. 2b and 4 show the same for the Uzen deposit.

Fig. 1 shows that the yield curves for Zhetybai petroleum have two distinct parts, which can be represented closely by means of the Shvedov—Bingham equation [7]:

$$\tau = 455 + 6.6 \cdot 10^3 \dot{\gamma} \ dyn/cm^2$$

for low shear rates and

$$\tau = 635 + 3.14 \cdot 10^2 \dot{\gamma} \ dyn/cm^2$$

for high rates (here and subsequently τ is the shear stress and $\dot{\gamma}$ is the shear rate in sec^{-1}).

There are essentially no peaks on the tangential-stress curves for $\dot{\gamma} < 3.5 \cdot 10^{-2}$, but the peaks become considerable for $\dot{\gamma} > 3.5 \cdot 10^{-2}$, while the flow curves in $\tau(\gamma)$ coordinates show inflections, which show that the structure changes when a shear stress τ^* is reached that corresponds to the inflection on the $\tau(\dot{\gamma})$ curve.

If the petroleum is considered as a dispersed system of coagulation type, it seems clear that the Zhetybai oil flows at low rates without structural alteration (structural state I), whereas at $\tau > \tau^*$ the structure is destroyed (structural state II).

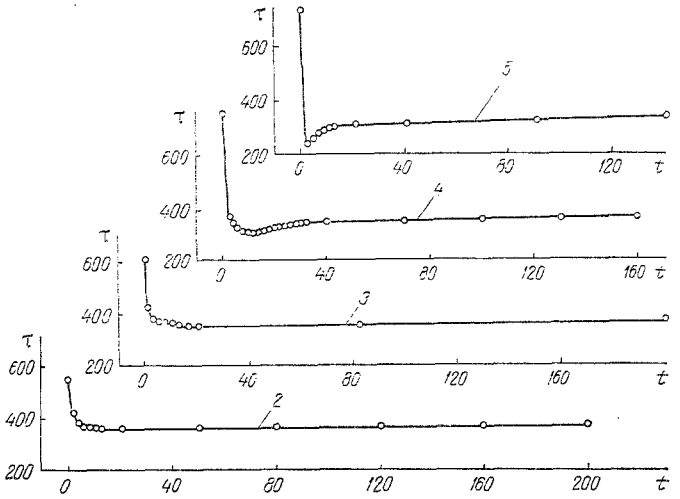

Fig. 3. Stress relaxation in Zhetybai petroleum after the attainment of steady-state flow (20°C) for shear rates (sec^{-1}) of: 2) $3.55 \cdot 10^{-3}$; 3) $1.12 \cdot 10^{-2}$; 4) $3.55 \cdot 10^{-2}$; 5) $1.12 \cdot 10^{-1}$).

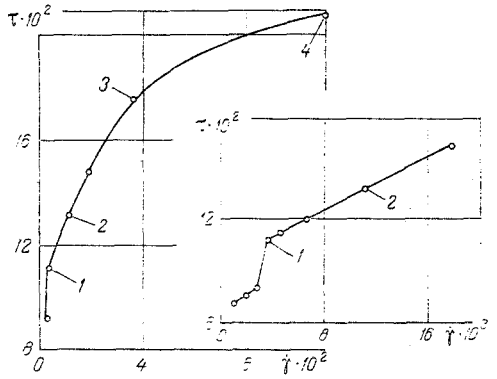

Fig. 4. Yield curves for Uzen petroleum; the numbers on the curves correspond to the symbols in Fig. 2; $\dot{\gamma}$ in sec^{-1}.

Thus, the difference between states I and II is that in the first case the solid phase (crystalline wax or asphaltene) is continuous, whereas in the second case it is discontinuous.

The thixotropic recovery is reflected in the relaxation after strain; the interpretation of the results of Fig. 3 is complicated by the need to consider the inertia in the working parts. When the strain ceases in state II, the motion of the plate reverses on account of the inertia in the tensioning device, and then the system may pass from state II to state I when the corresponding stress is attained.

However, the transition to state I does not mean that the system does not allow irreversible strain; there is a stress range $\tau^* - \tau_0^*$ (where τ_0^* is the critical stress for plastic strain) in which the relaxation is related to the plastic strain in the structure; the transition from I to II is not clear from the relaxation curves, but the point τ_0^* is identifiable, since the reverse motion of the plate at strains above τ_0^* is related to inertial effects. In the limit $t \to \infty$, equilibrium is reached between the elastic stresses in the structured petroleum and the elasticity of the tensioning system, so τ_0^* is the limiting value of τ for $t \to \infty$.

There are thus three stress ranges for Zhetybai petroleum as regards system response:

1) from 0 to τ_0^*, where the petroleum reacts as a solid;

2) from τ_0^* to τ^*, where there is irreversible deformation but retention of the structure (plastic strain);

3) $\tau > \tau^*$, where the petroleum flows as a dispersed system containing a discrete solid phase.

The rheology of Uzen oil differs from that of Zhetybai oil in that the effective viscosity is higher and the form of structural change is different (compare Figs. 1 and 4).

Uzen oil shows a maximum torque only slightly exceeding the value found for high shear rates (Fig. 2b), and the tangential-stress and flow curves indicate that there is no global change in the structure up to shear

TABLE 1. Relaxation Characteristics of Uzen Petroleum

$\dot{\gamma}$, sec^{-1}	τ_1, dyn/cm^2	θ_1, sec	τ_2, dyn/cm^2	θ_2, sec	τ_3, dyn/cm^2	θ_3, sec	τ_4, dyn/cm^2	θ_4, sec
$1{,}42\cdot10^{-3}$	—	—	149	4,06	144	50	605	2800
$3{,}55\cdot10^{-3}$	—	—	153	0,91	268	12	661	3220
$1{,}12\cdot10^{-2}$	373	1,0	162	8,90	87	34	689	7550
$3{,}55\cdot10^{-2}$	654	1,89	241	6,98	121	32	744	5600
$1{,}12\cdot10^{-1}$	769	1,24	327	4,44	289	32	695	3220
1,12	1576	0,87	446	3,56	266	42	461	3010

rates of about 0.1 sec^{-1}, i.e., this oil is in structural state I in this range of shear rates. The kink on the flow curve is related [8] to a form of work-hardening in the coagulation structure.

Shear rates above 0.1 sec^{-1} cause considerable structural alteration, although this is purely local; this is clear from the prolonged fall in the stress and from visual observation of the perturbed velocity distribution, which extends even to cracking and layering. The fall in the torque in that case occurs because the structure is damaged locally and the velocity distribution consequently alters, with the flow corresponding to the weakest parts (disrupted structure). This explains the considerable viscosity at high $\dot{\gamma}$. These features of Uzen oil are reflected in the relaxation curves, which were recorded in the same way as for Zhetybai oil and which were processed by the Bryukhanov—Tobol'skii method [9, 10], which gave the characteristic relaxation times.

The processing showed that the curves can be fitted by three or four exponentials, i.e., the shear stress is given as a function of time t by

$$\tau = \Sigma\tau_i \exp\left(\frac{-t}{\theta_i}\right) \quad \text{for} \quad i = 1,\ 2,\ 3,\ 4,$$

where θ_i is the relaxation time for characteristic process i, on the assumption of a discrete relaxation-time spectrum, while τ_i is a coefficient having the dimensions of shear stress whose magnitude indicates the contribution from relaxation process i.

Table 1 gives the results for τ_i and θ_i.

Uzen oil is deformed without complete destruction of the structure (conversion to a dispersed structure), as is clear also from the relaxation data; there are no minima on the $\tau(t)$ curves (Fig. 2b), while the importance of the relaxation times increases with the shear rate. There is a certain increase in τ_0* in the low range of shear rates (as is clear from the increase in τ_4 in Table 1), which is clearly due to a form of work-hardening. The rise in θ at shear rates up to $1.12\cdot10^{-2}$ sec^{-1} confirms this. As θ characterizes the plastic strain in the structured material, which itself is partly due to the previous strain and relaxation, the results must indicate that hardening at $\dot{\gamma} < 1.12\cdot10^{-2}$ sec^{-1} is accompanied by subsequent softening. Table 1 also shows that the importance of relaxation processes with short characteristic times increases with $\dot{\gamma}$. The reason is local disruption of the structure.

The following major characteristics of structured petroleum are required for practical purposes: The yield point τ_0, i.e., the stress at which flow starts in the prestationary stage; τ, the stress at which the structure is disrupted; and τ_0*, the stress characterizing the transition to the nonflowing state.

The petroleum does not differ in structural state before and after strain; repeated rheological tests on Uzen oil after storage for 3 months at 20°C showed that the flow curves were of the same general form as were those for the tangential stresses, but the values for the corresponding shear rates were increased by about a factor of 3. A fresh test on the same specimen after 2 h at rest gave similar values for the shear stresses, which also indicates that the deformation does not disrupt the coagulation structure.

The changes in rheology for Zhetybai oil after 2 h at rest were more substantial; detailed discussion of the effect falls outside the scope of the present paper, so we note only some particular features. The viscosity rises (by about a factor of 2 at low shear rates), and this is accompanied by a change in the shape of the tangential-stress curve and in the flow curve. The changes are such as to eliminate much of the difference in flow mechanism between the Zhetybai and Uzen specimens. In other words, after a period of rest, the continous solid phase has been largely restored from the discrete one, which applies to both types of oil. There is merely local failure in the structure, with the flow localized over the failed areas.

Major practical interest attaches to the structural state of the flowing oil, i.e., whether the measured effective viscosity in fact characterizes the system, as occurs with a fluid containing discrete phase, or whether

the results merely relate to the mode of flow in the particular instrument (with localized velocity distribution). It is clear that in the latter case any calculation should be based on the limiting stresses for a specimen of undisrupted structure, since the localization of the deformation in weakened areas, which is responsible for the fall in resistance, should be specific to this form of strain, particularly when the sense of strain is reversed.

The structural state of each of these specimens is thus dependent on many external factors, particularly the temperature, storage conditions, and previous state of strain, and therefore the rheology is substantially affected. The only way of incorporating the rheological behavior into production practice is to compare results from tests performed under identical conditions.

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ENTRANCE EFFECTS IN VISCOELASTIC FLUID FLOW IN CYLINDRICAL NOZZLES

V. Z. Volkov, V. D. Fikhman, G. V. Vinogradov, and A. I. Isaev

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The pressure losses prior to entry into a nozzle are determined in the flow of a viscoelastic medium in broad ranges of the viscosity and the discharge. A generalized dependence of the entrance pressure losses on the rate of shear is obtained in dimensionless form. An empirical equation is proposed for the computation of entrance pressure losses.

It is known that an "entry effect" [1], the crux of which is additional pressure losses in the plastic and elastic deformation of the medium during influx into the channel and in the shaping of the stream at the initial section of the channel, occurs in the flow of polymer solutions and melts in nozzles of finite length. The standard method of estimating the magnitude of the entrance effect at his time is the determination of the "entrance correction" according to Bagley [2], which is expressed as an additional fictitious nozzle length (in radii). However, in a number of papers [3], the correctness of the Bagley method is open to doubt. At the same time, an objective quantitative determination of the entry effect during the flow of polymer systems through a molding instrument is an actual scientific-technical problem whose solution is needed for the production of highly productive processes of polymer reworking.

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