THE INFLUENCE OF THE RATE OF DEFORMATION ON THE RATE OF THIXOTROPIC RECOVERY OF AN ALUMINUM NAPHTHENATE GEL AND A METHOD FOR OSCILLOGRAPHIC RECORDING OF STRESS-STRAIN CURVES

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Abstract

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THE INFLUENCE OF THE RATE OF DEFORMATION ON THE RATE OF THIXOTROPIC RECOVERY OF AN ALUMINUM NAPHTHENATE GEL AND A METHOD FOR OSCILLOGRAPHIC RECORDING OF STRESS-STRAIN CURVES

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It was shown earlier ([1,2]) that the thixotropic properties of gel-like systems can be evaluated from the increase in the yield strength P_r and the quasi-equilibrium value P_s^* during rest of the system after destruction of its structure.

The study of thixotropy must be based on the application of a destructive action to the system at some definite velocity gradient $\dot{\varepsilon}_{\text{destr}}$. This condition, however, was not observed in many investigations of thixotropy and was not recorded (for example, destruction of the structure of the system by the standard method in some stirrer was used). The subsequent measurement of the recovery of the structure must likewise be carried out at some definite velocity gradient $\dot{\varepsilon}_{\text{meas}}$. In this case the following two methods may be applied: 1) $\dot{\varepsilon}_{\text{destr}} = \dot{\varepsilon}_{\text{meas}}$ and 2) $\dot{\varepsilon}_{\text{destr}} \gg \dot{\varepsilon}_{\text{meas}}$. The use of both methods makes it possible to investigate the phenomenon of thixotropy rather completely and to draw a conclusion about the specific features of the structure of the system under study.

For the region of small ε, a quite reliable method for obtaining the curves $P(\varepsilon)$, characterizing the most important rheological properties of the system, is the compensation method, which ensures constancy of $\dot{\varepsilon}$ over the entire deformation interval (4). For larger $\dot{\varepsilon}$, in order to obtain such curves $P(\varepsilon)$, we developed an oscillographic recording procedure.

Fig. 1. Diagram of oscillographic recording of the curves $P(\varepsilon)$.
a –recording of P,
b –recording of ε and $\dot{\varepsilon}$

The scheme for recording the stress P or the angle of rotation of the inner cylinder φ in the method $\Omega = \text{const}$ (rotation of the outer cylinder with a specified speed) is as follows (Fig. 1a). A mirror 2 is fixed to the axis of the inner cylinder 1; onto it, from the illuminator 3 through the condenser 4 and the focusing lens 5, falls a beam of light of rectangular cross section,

Fig. 2. Oscillograms for aluminum naphthenate gel and printing ink No. 56.

Figure 1: Fig. 2. Oscillograms for aluminum naphthenate gel and printing ink No. 56.

Figure 3

Figure 2: Figure 3

by a slit 6 set on the illuminator. From the mirror the light beam is reflected onto the selenium photocell 7, the illuminated area of which is limited by a special rectangular frame. The photocurrent, proportional to the illuminated area, is fed to the loop of the oscillograph. The design of the instrument makes it possible to measure different limiting values of φ. In the present work the dynamometers were selected so that $\varphi \leqslant 5^\circ$, but in a number of cases φ was 2-3°, which, at a limiting deformation θ_r = 100-200°, practically ensured the condition $\dot{\varepsilon} = \text{const}$. On the same axis of the cylinder there is another mirror, which deflects the "spot" from the second illuminator 8 onto the scale 9, for visual reading.

Fig. 2. Oscillograms for aluminum naphthenate gel and printing ink No. 56.
1 –curves of change in the angle of twisting of the inner cylinder φ, 2 –recording of the angle of rotation of the outer cylinder θ, and 3 –recording of the time τ

a $-\dot{\varepsilon} = 1.45$, b $-\dot{\varepsilon} = 490.2$, c $-\dot{\varepsilon} = 152$, d $-\dot{\varepsilon} = 34.3$ s^{-1}

Of particular importance is the simultaneous recording on the film not only of φ (i.e., P), but also of the angle of rotation of the outer cylinder θ, i.e., the deformation ε and the rate of deformation $\dot{\varepsilon}$. The recording of ε is carried out as follows. On the axis of the cylinders 1 (Fig. 1b) is mounted a disk 4, rigidly connected with the cover 2 of the magnetic coupling 3. The disk has narrow radial slots every 20°, beneath which an illuminator 5 is placed. Above the slots is mounted a photocell 6, the photocurrent of which is fed to the loop of the oscillograph. The angle θ is recorded as peaks on the film. For example, $\varepsilon = \varepsilon_r$ is counted by the number of peaks up to $P = P_r$ of the curve $P(\varepsilon)$. Simultaneous recording of τ in the form of a sinusoid makes it possible to calculate also $\dot{\varepsilon}$ (Fig. 2).

Application of this method to a 2% aluminum naphthenate gel (factory experimental batch No. 24 (4)) in vaseline oil made it possible to reveal a number of new features of thixotropy in the region of medium and elevated $\dot{\varepsilon}$.

Figure 3a shows, as an example, the curves $P_r(\tau_{\text{rest}})$ and $P_s(\tau_{\text{rest}})$ for three $\dot{\varepsilon}_{\text{meas}}$, characterizing the recovery of the system structure after its breakdown at $\dot{\varepsilon}_{\text{br}} = \dot{\varepsilon}_{\text{meas}}$ (method I).

Fig. 3. Kinetics of thixotropic strengthening. a–at $\dot{\varepsilon} = 1.45$ s^{-1} (1), $\dot{\varepsilon} = 14.51$ s^{-1} (2), and $\dot{\varepsilon} = 490.2$ s^{-1} (3); 4–$\lg \tau_b = f(\lg \dot{\varepsilon})$; b–$\dot{\varepsilon} = 1.45$ s^{-1} (see explanation in the text)

The experiments were carried out as follows* (1). The completely recovered system was deformed with a prescribed $\dot{\varepsilon}$ and brought to $P = P_s$. After this the system was allowed to rest for a time τ_{rest}, and the measurement was repeated at the same $\dot{\varepsilon}_{\text{meas}} = \dot{\varepsilon}_{\text{br}}$. From the curves in Fig. 3a it is seen that with increasing $\dot{\varepsilon}$ the limiting maximum value $\Delta P = P_r - P_s$, which characterizes the thixotropic effect at each value of $\dot{\varepsilon}$, increases sharply. However, as $\dot{\varepsilon}$ increases, the time of complete recovery τ_b (the time for P_r to reach the horizontal portion of the curve) decreases; consequently, the rate of thixotropic recovery increases. For example, on going from $\dot{\varepsilon} = 1.45$ s^{-1} to $\dot{\varepsilon} = 1450$ s^{-1}, τ_b decreases from 10 h to 1 min. In logarithmic coordinates the dependence of τ_b on $\dot{\varepsilon}$ proves to be linear (Fig. 3a).

This result leads to the following conclusions:

1. The strength of the structure P_r at different $\dot{\varepsilon}_{\text{br}} = \dot{\varepsilon}_{\text{meas}}$ is determined by different structural elements, differing in the rate of their recovery.
2. The structural elements that provide P_r at smaller $\dot{\varepsilon}$ do not determine P_r at larger $\dot{\varepsilon}$. This, however, is not connected with irreversible destruction of the structure at larger $\dot{\varepsilon}$. The latter is confirmed by the coincidence of the values of τ_b (10 h) obtained at one and the same $\dot{\varepsilon}_{\text{br}} = \dot{\varepsilon}_{\text{meas}} = 1.45$ s^{-1} in two experiments (curve 1 in Fig. 3a and curve 1 in Fig. 3b), i.e., before and after measurement at all the $\dot{\varepsilon}$ indicated in Fig. 3a (curve 1 in Fig. 3b was obtained for a structure that had been recovering for a long time after previous actions on the system). It may be assumed that the more rapid recovery of the structure at larger $\dot{\varepsilon}$ is connected with the fact that the slowly recovering part of the structure is destroyed during the growth of P up to $P = P_r$.
3. The states of the structure corresponding to τ_b at different $\dot{\varepsilon}$ are not identical, despite the attainment of complete recovery of the structure with respect to P_r.

In addition to the reversible destruction of the structure considered, irreversible destruction of the structure may also occur in this system. Such destruction is detected from the decrease in the values of P_r and P_s, measured at small $\dot{\varepsilon} = 1.45$ s^{-1} before and after the action on the system of a large

* Radii of the cylinders: outer $R_2 = 1.500$ cm, inner $R_1 = 1.402$ cm.

of the velocity gradient $\dot{\varepsilon}$ (curve 1 in Fig. 3a and curve 1 in Fig. 3b, as well as curves 1 and 2* in Fig. 3b). In this respect an analogy may be drawn with ideas about condensation and dispersion structures in solid-plastic systems ([3]).

Irreversible destruction of the structure may also occur as a result of aging of the system; this is manifested in a decrease of P_r and P_s on curve 3 in Fig. 3b, obtained by method I after an aging time $\tau_{\text{st}} \approx 1$ month, as compared with curve 2 in Fig. 3b. The small value of τ_v is mainly associated with the use of method I.

Fig. 4

Figure 3: Fig. 4

The dependence of the magnitude of the deformation ε_r, determined from the maximum stress P_r on the curve $P(\varepsilon)$, on the change in $\dot{\varepsilon}$ is of interest (Fig. 4). Even at those small $\dot{\varepsilon}$ for which a maximum P_r appears on the $P(\varepsilon)$ curve, the value of ε_r proves to be the greatest, $\sim 6200\%$ (average value). It remains constant over a certain interval of $\dot{\varepsilon}$ (or P_r), but then, beginning with the comparatively small $\dot{\varepsilon} = 1.45$ s^{-1}, decreases appreciably. When $\dot{\varepsilon}$ changes from 1.45 s^{-1} to 1450 s^{-1}, ε_r decreases by approximately a factor of 2. The rupture deformation ε_r may include elastic, highly elastic, and irreversible plastic deformation. An increase in $\dot{\varepsilon}$ may lead to a decrease in plastic deformation as a result of weakened relaxation. At sufficiently large $\dot{\varepsilon}$, the highly elastic deformation may also decrease because coil-like folded particles will not have time to unfold owing to the influence of aftereffect viscosity and will rupture, as it were, prematurely. It may be supposed that the observed decrease in ε_r at small $\dot{\varepsilon}$ occurs mainly at the expense of a decrease in irreversible deformation, while at the largest $\dot{\varepsilon}$ the second mechanism becomes predominant. Difficulty in the unfolding of coils can probably occur for any highly elastic system, but the values of $\dot{\varepsilon}$ corresponding to the decrease in ε_r for this reason will be the higher, the more mobile the structural elements and the smaller the aftereffect viscosity η_τ.

Fig. 4. Dependence of ε_r and P_r (the values of P_r change in the same direction as $\dot{\varepsilon}$)

It was also noted that the rupture deformation ε_r decreases with an increase in P_r during thixotropic recovery of the structure (for example, at $\dot{\varepsilon} = 1.45$ s^{-1}, from 7300% to 5400%).

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* Curve 2 in Fig. 3b was obtained by the method II indicated above, under conditions where

$$\dot{\varepsilon}_{\text{destr}} = 1450 \text{ s}^{-1} \gg \dot{\varepsilon}_{\text{meas}} = 1.45 \text{ s}^{-1}.$$

In this case the structure of the system was destroyed (at $\dot{\varepsilon}_{\text{destr}}$) before each τ_{rest}. The peculiarity of this method of measuring thixotropy, in contrast to method I, is manifested in an increase of τ from 10 h to 40 h.

Note: Figure translations are in progress. See original paper for figures.