3. A. Peterlin, Z. Phys., 111, 232 (1938).
4. H. A. Scheraga, J. Chem. Phys., 23, 1526 (1955).
5. Yu. I. Shmakov, E. Yu. Taran, and P. B. Begoulev, Hydromechanics [in Russian], No. 20, Naukova Dumka (1972), p. 87.
6. H. L. Goldsmith and S. G. Mason, J. Coll. Sci., 17, 448 (1962).
7. B. S. Petukhov, Heat Exchange and Resistance during Laminar Fluid Flow in Pipes [in Russian], Énergiya, Moscow (1967).
8. V. N. Tsvetkov, V. E. Éskin, and S. L. Frenkel', Macromolecule Structure in Solutions [in Russian], Nauka, Moscow (1964).
9. D. Lans, Numerical Methods for High-Speed Computers [Russian translation], IL, Moscow (1962).

VISCOELASTIC BEHAVIOR OF MINERAL OILS AT HIGH PRESSURE

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Results of an experimental study of shear viscoelasticity of mineral oils and a method for approximating liquid relaxation spectra by a generalized Maxwell model are presented.

The stressed state of an oil layer in a heavily loaded rapidly moving elastohydrodynamic friction-pair contact can be described by the assumption of delay in establishment of equilibrium viscosity upon a sharp change in pressure in the contact zone [1, 2, 3].

The representation of liquid structural equilibrium-delay processes by the Frenkel'–Obraztsov model for gradual pressure change [2] leads to the expressions for viscosity at the contact:

$$\eta = \eta_0 \exp \alpha P_1 \exp(-\beta\alpha P_1) \tag{1}$$

and delay time:

$$t_{\mathrm{ret}} = \frac{\eta_0}{G_\infty} \exp \alpha P_1. \tag{2}$$

The parameter β is defined in [2] from the equation

$$\frac{G_\infty t}{\eta_0 \exp \alpha P_1} = \mathrm{Ei}(\beta\alpha P_1) - \mathrm{Ei}(\beta_1 \alpha P_1). \tag{3}$$

Here $\mathrm{Ei}(\beta_1 \alpha P_1)$ is an exponential integral, which considers the loading prehistory.

In Eqs. (2) and (3) there appears the value of the instantaneous shear modulus of elasticity G_∞, which can be obtained from study of liquid relaxation spectra.

It is known [4] that mineral oils have continuous relaxation spectra encompassing not less than 5-8 frequency decade. A phenomenological representation of this behavior in mineral oils is possible within the framework of the generalized Maxwell model. For this model the most general form of the complex modulus of elasticity expanded into the relaxation time spectrum was employed:

$$G = G_\omega + jG_N = \sum_{i=1}^{n} \frac{\omega^2 \tau_i^2}{1 + \omega^2 \tau_i^2} G_i + j\omega \sum_{i=1}^{n} \frac{\eta_i}{1 + \omega^2 \tau_i^2}. \tag{4}$$

The components of the complex modulus of elasticity G_ω and G_N were measured at pressures to $6 \cdot 10^8$ N/m^2 at temperatures of 17-100°C by quartz torsional oscillation resonators at frequencies of 23, 43, 80, and 126 kHz by the method described in [5]. Since this frequency interval does not include the range

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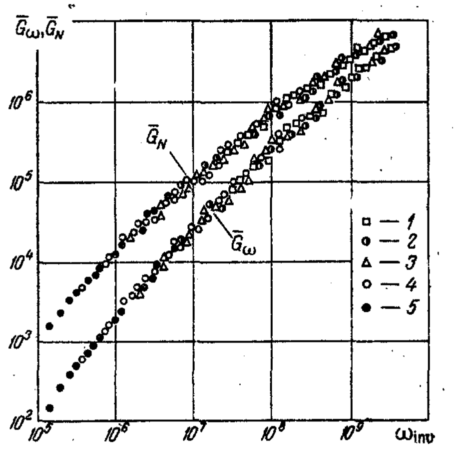

Fig. 1. Frequency distribution of components of complex shear modulus for MS-14 oil, obtained by reduction with respect to temperature and pressure: 1) 17.2°C; 2) 34.3°C; 3) 50°C; 4) 74°C; 5) 100°C. G_ω, $\bar{G}_N$, N/m^2; ω_{inv}, 1/sec.

necessary for study of the spectra of the oils, the frequency range of G_ω and G_N measurement was expanded by the method of reduction of variables [4, 6]. Pressure and temperature reductions were made to atmospheric pressure and temperature $T_0 = 100°C$. The temperature and pressure correction coefficients $a = \eta_{T,P}/\eta_{T_0,0}$ for the oils were determined from the formula

$$a = \exp[-\beta_0(T - T_0) + \alpha_T P). \tag{5}$$

The validity of this formula is confirmed by comparison of calculated data with experimental data for 30 oil specimens of differing hydrocarbon composition, studied at pressures up to $6 \cdot 10^8$ N/m^2 and at temperatures of 20-125°C.

It was established that for oils with polymer-thickening additives in weight concentration up to 20%, with molecular weights up to 30,000, the correction coefficient is determined basically by the temperature and piezocoefficients of viscosity of the solvent-bases.

An example of a relaxation spectrum, obtained by the method of reduction of variables from measurements at 23, 43, 80, and 126 kHz at pressures up to $6 \cdot 10^8$ N/m^2 in the temperature range 17-125°C, is presented in Fig. 1 for MS-14 oil. In the figure $\omega_{inv} = a\omega$ is the corrected frequency.

As a rule, in the oils studied the relationship between $1/\eta_\omega$ and ω^2 was not linear, and so it may be assumed that relaxation spectra exist in them [7]. The relaxation spectra obtained were approximated by the generalized Maxwell model with the use of Eq. (4).

The approximation was performed with an electronic computer by searching for the minimum in the mean-square deviation S of the functions $G_\omega = F_1(\omega, G_i, \tau_i)$ and $G_N = F_2(\omega, G_i, \tau_i)$ from the values of $\bar{G}_\omega(\omega)$, $\bar{G}_N(\omega)$ in the corrected spectral curves for arbitrary values of G_i and τ_i.

The relative mean-square deviation was defined in the form

$$S = \sqrt{\frac{1}{2m}\left\{\sum_{K=1}^{m}\left[\frac{\bar{G}_\omega(\omega_K) - G_\omega(\omega_K, G_i, \tau_i)}{\bar{G}_\omega(\omega_K)}\right]^2 + \sum_{K=1}^{m}\left[\frac{\bar{G}_N(\omega_K) - G_N(\omega_K, G_i, \tau_i)}{\bar{G}_N(\omega_K)}\right]^2\right\}}. \tag{6}$$

Here $\bar{G}_\omega(\omega K)$ and $\bar{G}_N(\omega K)$ are ordinates in the K-th sections with abscissas $(\omega K)_{inv}$ of the curves obtained by reduction of variables.

The search for the minimum of the relative mean-square deviation was performed by the configurations method [8].

Expansion (4) is a special case of a rational function. The accuracy with which the approximating function approaches the true values of the functional dependence is determined [9] by the degree of the n-polynomial in the denominator of the fraction (in the given case, n is the number of relaxation mechanisms in the

TABLE 1. Oil-Relaxation-Spectrum Approximation by Generalized Maxwell Model

n	G_i, N/m² m²	$\tau_i \times 10^7$ sec	S, %	$\eta_{100^\circ,0}$ N·sec/m², experim.	$\eta_{100^\circ,0} = \sum_{i=1}^{n} G_i\tau_i$, N·sec/m²	$\frac{\eta_{100^\circ,0} - \sum_{i=1}^{n} G_i\tau_i}{\eta_{100^\circ,0}} \cdot 100\%$	$G_\infty = \sum_{i=1}^{n} G_i\tau_i$, N/m²	$(\tau^S)_{T_\bullet,0} \times 10^8$ sec
MS-14 oil								
1	2403506	0,116	156		0,0278	112	2403505	
2	4955578	0,015						
	14151	5,39	45,9		0,0149	13	4969730	
	6837115	0,007		0,0131				
$n_{\text{lim}}=3$	156988	0,321	20,2		0,0139	6	6996416	0,200
	2312	17,50						
MS-20 oil								
1	373201	0,613	12,6		0,0249	46,5	373201	
2	208651	0,595	10,1		0,0247	46	415945	
	207293	0,485						
	243775	0,0664		0,0173				
3	48579	2,460	8,2		0,0223	30	1781566	1,25
	1489212	0,074						
	197125	0,0287						
$n_{\text{lim}}=4$	50694	2,427	8,2		0,0220	29	2300190	
	1142434	0,0635						
	909934	0,0509						
Specimen P-37 (base G-14+20% vinypol)								
1	861992	0,136	24		0,0118	38,8	861992	
2	56288	1,348	4,6		0,0112	30	1038224	
	981936	0,0411		0,0085				
	70323	1,090						
$n_{\text{lim}}=3$	1039769	0,0360	4,0		0,0102	20	1110664	1,06
	572	0,00014						

generalized Maxwell model). Since, at present, general criteria for limitation of the power n are not known, in estimating the accuracy of approximation of the rational function, one usually approaches the selection of n subjectively, commencing with the least complex approximating function.

The determination of the power n in expansion (4) may be performed by considering the minimum of the mean-square deviation S at the maximum correspondence of measured static viscosity η with the calculated value:

$$\eta = \lim_{n\to\infty} \sum_{i=1}^{n} G_i\tau_i. \tag{7}$$

However, the tendency to complete convergence of measured and calculated viscosities attainable with increase of n in expansion (4) can lead to the appearance of noise in the calculated coefficients of the approximating function. The latter is due to random errors in measurement and extrapolation errors in correcting the viscosity.

A reliable approximation of the relaxation spectra of the oils by expansion (4) with minimum machine-time expenditure is possible if n is limited by the convergence moment of the right and left sides of the inequality

$$\frac{\eta_{T_\bullet,0}}{\sum_{i=1}^{n} G_i\tau_i} \leqslant 1+\delta\eta_{T,P}. \tag{8}$$

Here $\delta\eta_{T,P}$ is the limiting error in viscosity reduction with use of Eq. (5). For all oils studied the error $\delta\eta_{T,P}$ does not exceed 0.3.

An example of relaxation-spectrum approximation for three oils with the generalized Maxwell model is presented in Table 1. In the table, n_{lim} is the limiting number of Maxwell mechanisms in the generalized model, found from the condition of Eq. (8). It is evident from the table that with increase in n for all oils, the mean-square deviation S decreases and Eq. (7) converges. Table 1 shows values of mean phenomenological relaxation times $(\tau^S)_{T_0,0}$, determined for atmospheric pressure and a correction temperature of 100°C from the expression $(\tau^S)_{T_0,0} = \eta_{T_0,0}/G_\infty$. In calculating $(\tau^S)_{T_0,0}$, the instantaneous modulus G_∞ is defined in the form

$$G_\infty = \sum_{i=1}^{n_{\lim}} G_i.$$

Calculations of shear relaxation time and the delay time of equilibrium-viscosity establishment at pressures of $1.5 \cdot 10^9 - 3 \cdot 10^9$ N/m² in the temperature interval 20-125°C show that these times for the oils studied will lie in the interval 10^{-5}-10^{-2} sec. Such high delay times for establishment of equilibrium viscosity with instantaneous volume compression indicate the necessity of considering volume viscoelastic effects in corresponding hydrodynamic calculations of rapidly moving friction-pair contacts.

NOTATION

α, piezocoefficient of viscosity in Barus equation $\eta_P = \eta_0 \exp \alpha P$; β_0, temperature coefficient of viscosity at atmospheric pressure; G_∞, instantaneous modulus of elasticity; η_0, static viscosity at atmospheric pressure; P_1, pressure equal to maximum Hertz stress in contact; $\beta = 1 - (P^*/P_1)$, parameter; P^*, fictitious pressure corresponding to change in free volume for time $t > 0$ upon action of pressure P_1 after its abrupt change; $\mathrm{Ei}(\beta\alpha P_1)$, $\mathrm{Ei}(\beta_1\alpha P_1)$, exponential integrals; t_{ret}, delay time for establishment of equilibrium viscosity; τ, Maxwell relaxation time; G_ω, dynamic modulus of elasticity; G_N, loss modulus; η_i, G_i, τ_i, viscosity, modulus of elasticity, and relaxation time of i-th relaxation mechanism; ω, circular frequency; a, temperature and pressure correction coefficient; ω_{inv}, corrected frequency; $\overline{G}_\omega$, $\overline{G}_N$, dynamic and loss moduli corrected to atmospheric pressure and correction temperature T_0; $\eta_{T_0,0}$, static viscosity at atmospheric pressure and correction temperature T_0; $\eta_{T,P}$, static viscosity at pressure P and temperature T; $\eta_\omega = G_N/\omega$, dynamic viscosity; S, relative mean-square deviation; n, number of relaxation mechanisms in generalized Maxwell model; $n_{\lim}$, limiting number of relaxation mechanisms sufficient for reliable approximation of relaxation spectra by generalized Maxwell model.

LITERATURE CITED

1. J. C. Bell and J. W. Kannel, "Interpretation of data on oil film thickness with vibration. Parts 1 and 2," in: Friction and Lubrication Problems [Russian translation], Ser. F, No. 4, Mir (1971).
2. R. S. Fein, J. Lubrication Technol., Trans. ASME, Ser. F, 89, No. 2 (1967).
3. G. Harrison and J. G. Trachman, "The role of viscoelastic compression in lubrication of rolling contacts," in: Friction and Lubrication Problems [Russian translation], Ser. F, No. 4, Mir (1972).
4. A. J. Barlow and J. Lamb, J. Proc. Roy. 253, 52-69 (1959).
5. B. P. D'yanchenko, Author's Abstract of Candidate's Dissertation, S. P. Korolev Aviation Institute, Kuibyshev (1973).
6. J. D. Ferry, Viscoelastic Properties of Polymers, 2nd ed., Wiley (1970).
7. I. G. Mikhailov, V. A. Solov'ev, and Yu. P. Syrnikov, Fundamentals of Molecular Acoustics [in Russian], Nauka, Moscow (1964).
8. D. J. Wilde, Optimum-Seeking Methods, Prentice-Hall (1964).
9. R. W. Hamming, Numerical Methods for Scientists and Engineers, McGraw-Hill (1962).