CAPABILITIES OF THE DYNAMIC QUARTZ-RESONATOR METHOD FOR DETERMINING THE VISCOELASTIC PARAMETERS OF THIN LIQUID LAYERS

V. Yu. Naumenko,[a] **N. N. Firsov,**[a] **R. A. Turusov,**[b] **and N. V. Klimova**[a]

The capabilities of the dynamic quartz-resonator method for determining the viscoelastic properties of liquids in thin layers (to 1 μm) have been studied. Aqueous solutions of glycerin of different concentrations and motor oils of different manufacturers have been used. The process of polymerization of ED-22 epoxy adhesive in the presence of a hardener — polyethylene polyamine — has been investigated as the model experiment. It has been shown that the broadening of the resonant curve and the shift of the resonant frequency plotted as functions of the thickness of a liquid layer enable one to single out the elastic and viscous components; this makes it possible to judge the change in the structure of boundary layers with processes that may occur at the interphase boundary.

An analysis of the interrelation between the structure and the properties of molecules of a liquid at the interphase boundary is one fundamental trend in modern science. When a liquid layer is placed on a solid surface, the liquid's boundary layer is exposed to the field of this surface [1–3]. The interaction between the molecules of the boundary layer and the molecules of the solid is direct and the strongest. The asymmetry of forces of interaction between the molecules of the interphase layer and the surrounding molecules is responsible for the existence of tangential forces and those normal to the interface of (surface-tension and molecular-pressure) forces acting on the transition-layer molecules. The fields of solid surfaces, when a liquid layer is placed between them, act on the physical properties of boundary layers and, passing through a boundary layer, determine the attraction interaction of the solid surfaces. Thus, the normal and tangential interaction forces (adhesion-cohesion and frictional forces) must be dependent on the thickness of boundary layers. The boundary-friction force must increase with decrease in the layer thickness.

As the experiments carried out show [4], the viscosities of the films of lubricants, retained in nanogaps, are orders of magnitude higher than the viscosities of the lubricants in a macroscopic volume. For lubrication of surfaces for a high velocity of motion one usually uses a non-Newtonian fluid. Therefore, it becomes necessary to carry out experimental investigations for high deformation rates.

Materials and Methods. Experimental determination of the mechanical parameters of a boundary liquid layer is very difficult. One method allowing for intermolecular interaction is the dynamic quartz-resonator method [5–7]; the quartz resonator contains a crystal of piezoelectric quartz (piezoquartz) with pronounced resonance properties and a Q factor of the order 10^5 as the detector-transducer. This method has been successfully used in different versions for investigating the surface properties of solids and liquids [8–10].

A block diagram of the quartz resonator is shown in Fig. 1. A piezoquartz crystal 1 whose geometric parameters are equal to $30 \times 15 \times 6$ mm is installed between two steel elements 2 and 3 capable of moving relative to each other vertically using a worm mechanism 4. The piezoquartz is clamped with steel needles 5 located in the nodal plane of its vibrations using spring 6 and screw 7 and is placed between two pairs of electrodes of capacitors 8 and 9. The first pair of plates of the capacitor 8 is used for feeding electric voltage; the voltage excites longitudinal mechanical vibrations in the piezoquartz, using the inverse piezoeffect. The piezoquartz 1 induces a potential difference
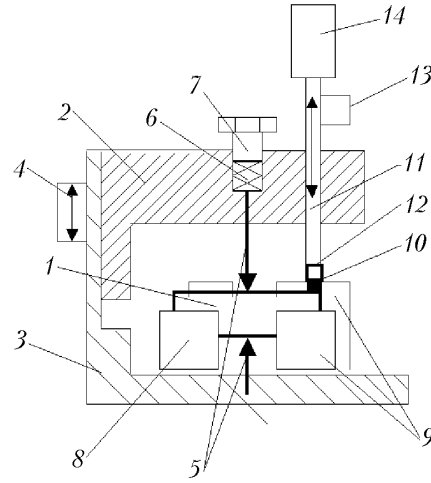
Fig. 1. Diagram of a quartz resonator.

on the second pair of plates of the output capacitor 9; the potential difference is recorded in the form of a resonant curve with change in the exciting-generator frequency and is fed to the input of a computer for subsequent processing. The size of the gap between the plates of the capacitors 8 and 9 and the lateral piezoquartz surfaces is 0.2 mm.

A liquid sample 10 in the form of a 5 μl droplet is placed on the surface of the piezoquartz 1 and is tightened up by a vertically movable rod 11 with the quartz cylindrical prism 12 adhered to its end. The gap between the elements 1 and 12 is provided by the mechanisms of rough 4 and precise 13 positioning, manufactured in the form of worm-and-worm and screw pairs respectively. The width of this gap is measured by optimeter 14 accurate within 0.5 μm.

The main idea of measurements is as follows. When the sample under study is imposed on a vibrating piezoquartz surface, the resonant frequency and the shape of the resonant curve of the quartz resonator change. The resonant frequency of a free piezoquartz is determined by the relation

$$\omega^2 = \frac{k_0}{M} - 2\beta_0^2 . \tag{1}$$

In the case of forced vibrations the principle of superposition of vibrations, in which vibrations caused by different forces are mutually independent, is valid [11]. Then upon the application of the material of mass m under study on the piezoquartz surface, the resonant frequency of the quartz resonator will be another now:

$$\omega_{\text{load}}^2 = \frac{k_0 + k}{M + m} - 2\beta_{\text{load}}^2 . \tag{2}$$

Assuming that $\omega_{\text{load}} + \omega \approx 2\omega_0$ and $\beta_0 \approx 0$ and subtracting expression (1) from Eq. (2), we obtain

$$2\omega_0 \Delta\omega = \frac{k}{M + m} - \frac{m\omega_0^2}{2(M + m)} - \beta_{\text{load}}^2 . \tag{3}$$

Passing to the linear frequency $f_0 = \omega_0/2\pi$ and taking into account that $m \ll M$, we determine the resonant-frequency Δf shift in the form

$$\Delta f = \frac{k}{8\pi^2 M f_0} - \frac{m f_0}{2M} - \frac{\beta_{\text{load}}^2}{4\pi^2 f_0} . \tag{4}$$

From an analysis of Eq. (4) it follows that the resonant-frequency shift will be a positive quantity, if the interphase layer possesses a shear elasticity k, and the second and third terms are smaller than the first term.
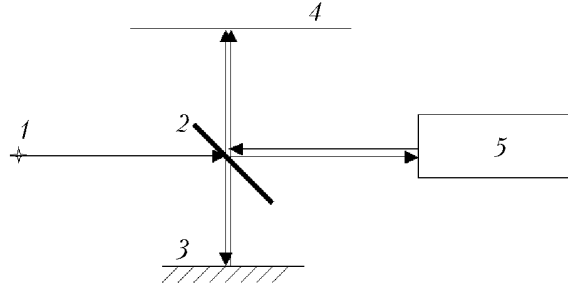
Fig. 2. Optical scheme for determination of the vibration amplitude of piezoquartz.

For a Newtonian fluid having no elasticity ($k = 0$) the frequency shift will take on a negative value; in this case we have

$$\Delta f = -\left(\frac{mf_0}{2M} + \frac{\beta_{\text{load}}^2}{4\pi^2 f_0}\right). \tag{5}$$

The first term on the right-hand side of the equation is determined by the fluid mass m entrained by the vibrating piezoquartz surface, whereas the second is characterized by the dissipation energy or viscosity.

According to vibration theory, the damping factor of free piezoquartz is determined as

$$\beta_0 = \frac{R_0}{2M} = \pi \Delta F_0, \tag{6}$$

and, with allowance for the fluid layer, will be equal to

$$\beta_{\text{load}} = \frac{R_0 + R}{2(M + m)} = \pi \Delta F_{\text{load}}. \tag{7}$$

Combining Eqs. (6) and (7) and assuming that $m \ll M$, we obtain an expression for the coefficient of resistance of the fluid layer in the form

$$R = 2\pi M (\Delta F_{\text{load}} - \Delta F_0) = 2\pi M \Delta F. \tag{8}$$

For a viscous fluid the coefficient of resistance is equal to

$$R = \frac{\eta S}{H}. \tag{9}$$

Simultaneous solution of Eqs. (8) and (9) for the coefficient of viscosity leads to the expression

$$\eta = \frac{2\pi M}{S} \frac{\Delta F}{1/H}. \tag{10}$$

In the experiment, we determined two independent quantities: Δf characterized by the elasticity of the layer and ΔF determined by the dissipative loss or viscosity. It is noteworthy that these quantities are dependent on the number of adhesion bonds that have formed molecular contacts.

Determination of the values of amplitudes in feeding an excitation signal is significant in the case of mechanical vibrations of piezoquartz. The amplitude of mechanical piezoquartz vibrations was measured by an interference method analogous to that based on the Michelson interferometer; its scheme is shown in Fig. 2.

Monochromatic light from a laser source 1 whose wavelength is 632.8 nm is split by a semitransparent plate 2 into two beams. One is reflected from mirror 3 and is transmitted by the plate 2 again; thereafter it arrives at screen 4.
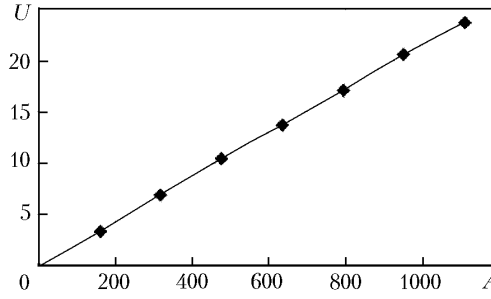
Fig. 3. Voltage tapped off from the output plates of the quartz resonator vs. vibration amplitude of piezoquartz. U, V; A, nm.

The second beam reaches the end surface of piezoquartz 5, is reflected from this surface, and, being transmitted by the plate 2, arrives at the screen 4, too. The two beams create, on the screen 4, a clear interference pattern where the difference of their paths corresponds to the condition

$$L_1 - L_2 = \lambda n . \tag{11}$$

Monochromatic light from the laser source 1 makes it possible to create the interference pattern for large path differences and requires little adjustment of the initial path difference. When the end piezoquartz surface is periodically displaced perpendicularly to the beam incident onto it by the law $A = A_0 \cos \omega t$, the contrast of the interference pattern will change.

Each value of the amplitude of vibrations of the end piezoquartz surface will correspond to its beam-path difference that will change with a frequency equal to a piezoquartz-vibration frequency of 72 kHz. The interference pattern will change with the same frequency. These changes are perceived by the eye as a certain average state that corresponds to either a clear interference pattern having light-intensity maxima and minima or a monotonic intensity distribution; the pattern becomes indistinct, i.e., "blurred." When the piezoquartz-vibration amplitude is equal to

$$A = n \frac{\lambda}{2} , \tag{12}$$

the interference pattern will be perceived as clear, otherwise it becomes blurred.

The method of measurement is as follows. The amplitude of mechanical vibrations of piezoquartz increases with electric voltage fed by the system. Gradually increasing the amplitude, from successive blurrings of the interference pattern we determine the piezoquartz-vibration amplitude which will increase by $\lambda/2$ each time.

The voltage induced by piezoquartz on the output plates of the capacitor in the next blurring of the interference pattern is recorded by a digital voltmeter. The latter is necessary for determining the vibration amplitude of piezoquartz from a calibration chart (Fig. 3) directly during the experiment. The digital voltmeter makes it possible to measure the voltage tapped off directly from the output quartz-resonator plates with an error no higher than 0.1 mV.

Results and Discussion. As the model experiment, we consider polymerization of ED-22 epoxy adhesive in the presence of a polyethylene-polyamine (PEPA) hardener. When the epoxy adhesive is in a liquid state between two solids, the adhesion force is predominant in interaction between the adhesive molecules and the solid surface. The adhesive molecules are adsorbed at fixation sites on the surface under the action of surface forces and form the area of molecular contact.

In the general case the adhesion strength of contact is dependent on the strength of a single adhesion bond and on the number of bonds per unit surface. The number of bonds in turn is dependent on the structure of a boundary layer and on the dimensions of kinetic units and the density of their packing.

Figure 4a gives the experimental dependences of the resonant- frequency shift Δf of piezoquartz on the time of the process of polymerization of an adhesive-bonded joint. The negative resonant-frequency shift Δf is determined by the process of formation of molecular contact and by the value of a certain mass m entrained by the vibrating surface of the quartz crystal according to Eq. (5). From an analysis of Fig. 4a it follows that the duration of formation of molecular contact increases with adhesive-layer thickness H, and the position of the Δf minimum shifts to the right.
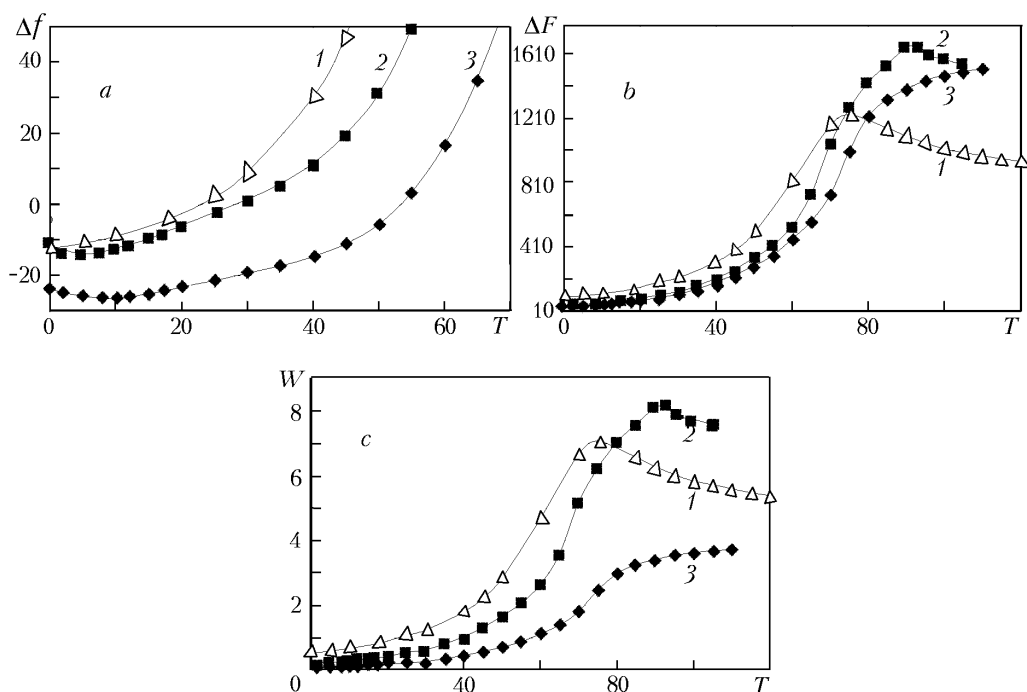
Fig. 4. Resonant-frequency shift Δf (a), relative broadening of the resonant curve ΔF (b), and loss-energy density W (c) vs. time of polymerization of the adhesive for adhesive-layer thicknesses H of 1) 30; 2) 70; 3) 140 μm. Δf and ΔF, Hz; W, J/m^3; T, min.

The process of polymerization occurs earlier for smaller thicknesses of the adhesive layer: when $H = 30$ μm, it begins almost instantaneously with application of the adhesive on the surface; when $H = 70$ and 140 μm this takes 5 and 10 min, respectively. In Fig. 4a, it is seen that, for an adhesive-layer thickness of 30 μm, the quantity Δf intersects the abscissa axis within 22 min, whereas for layer thicknesses of 70 and 140 μm, such an intersection is observed within 28 and 53 min after the application of the adhesive respectively.

The forces of intermolecular interaction (cohesion forces) begin to grow with adhesive polymerization; the elasticity of bonds grows, which leads, according to Eq. (7), to growth in Δf with polymerization time. Furthermore, an analysis of the same equation shows that, as the layer thickness H decreases, the values of the resonant-frequency shift Δf must be higher, all other things being equal, which is in complete agreement with the behavior of the dependences of Δf in Fig. 4a.

The relation of the relative broadening of the resonant curve ΔF characterizing the energy dissipation in the boundary adhesive layer to the time of its polymerization is given in Fig. 4b. The ΔF values increase with polymerization time for all the layer thicknesses indicated above. It follows from the figure that ΔF for an adhesive-layer thickness of 30 μm lies higher than that for other layer thicknesses and attains its maximum ($\Delta F = 1220$ Hz) within 75 min after the application of the adhesive layer. As the layer thickness increases, the ΔF curves lie lower, and the positions of the ΔF maxima shift toward longer times.

The kinetics of the loss-energy density W is presented in Fig. 4c. The behavior of these curves confirms that, in a thinner layer, the quantity W at the initial time intervals is higher, which, probably, leads to a somewhat larger heating of this layer and to an acceleration of the process of polymerization. As the layer becomes thicker, the slope of the plots decreases, the kinetic curves lie lower, and the position of the W maximum shifts toward longer times. For an adhesive-layer thickness of 140 μm, the density of the energy scattered in the adhesive-layer volume after 80 min of polymerization is much lower than that for thinner layers,

The adhesive loses its fluidity in the process of polymerization and a rapid growth in the stresses in the boundary layer begins, which increases the probability of separation of overstressed adhesion bonds and accordingly decreases the number of bonds on a unit surface area.
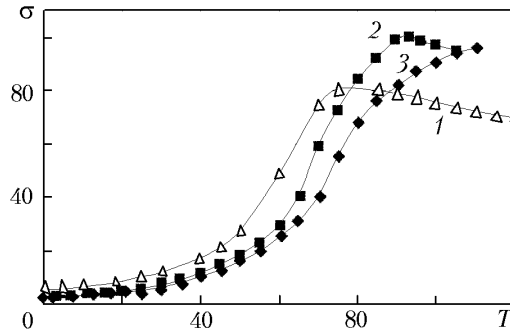
208

Fig. 5. Kinetics of shear stress for the adhesive layer of thickness H equal to:
1) 30; 2) 70; 3) 140 μm. σ, kPa; T, min.

TABLE 1. Coefficient of Viscosity and Shear Elasticity of the Aqueous Solutions of Glycerin

C, % glycerin	G, kPa	$\eta \cdot 10^{-3}$, Pa·sec	
		$\dot{\gamma} = 570 \text{ sec}^{-1}$	$\dot{\gamma} = 2200 \text{ sec}^{-1}$
Water	159.7	1.10	2.28
1	219	1.21	2.63
5	274	1.47	2.92
10	358	1.58	3.07
20	552	1.84	3.53
30	707	2.45	4.38
50	942	3.73	6.57

When the layer thickness is smaller, the angle of shear γ grows, which leads to an increase in the loss-energy density and an increase in the number of separation of bonds. This is responsible for the presence of the maxima of the corresponding dependences presented in Fig. 4c. The decrease in the number of adhesion bonds in turn causes microvoids to form in the boundary volume and the internal stresses to be redistributed. In deformation of the interphase boundary of a thinner adhesive layer, in the process of its polymerization, the temperature increases and the loss-energy density grows at these sites of overstresses or local interface points (Fig. 4c).

Thus, in deformation of the adhesive-bond joint, in the process of its polymerization, we have a buildup of the stresses and a widening of the distribution function of the adhesion bonds by their inhomogeneity, which leads to a lower strength of the adhesive-bonded joint. This also follows from the given results of the kinetic dependences of the shear stresses σ (Fig. 5). Thus, for a layer thickness of 30 μm, the position of the σ maximum is observed at shorter polymerization times than that for other thicknesses, and in shear deformation the process of separation of bonds begins earlier, which is characterized by the decrease in σ.

The strength properties of the adhesive on a solid surface are determined by the influence of the surface forces of this surface.

It is possible that, when the deformation of the boundary adhesive layer is absent, the thinner the adhesive layer, the smaller will be the change in the number of adhesion bonds and the generated stresses, which, probably, must lead to an increase in the breaking strength.

The foregoing shows that the dynamic quartz-resonator method makes it possible to measure the mechanical parameters of both liquid bodies and solids. To demonstrate the capabilities of the dynamic quartz-resonator method for measuring the viscoelastic parameters of liquid bodies, we took a glycerin solution diluted in distilled water (Table 1). Figure 6 plots the relative broadening ΔF of the resonant curve and the shift of the piezoquartz resonant frequency Δf as functions of the thickness of the film of the aqueous solution of glycerin for different concentrations. For distilled water, the dissipative loss characterized by the quantity ΔF and determined by viscosity grows with decrease in the film thickness, since the rate of shear grows. Upon the addition of the glycerin solution to it, the ΔF plots lie the
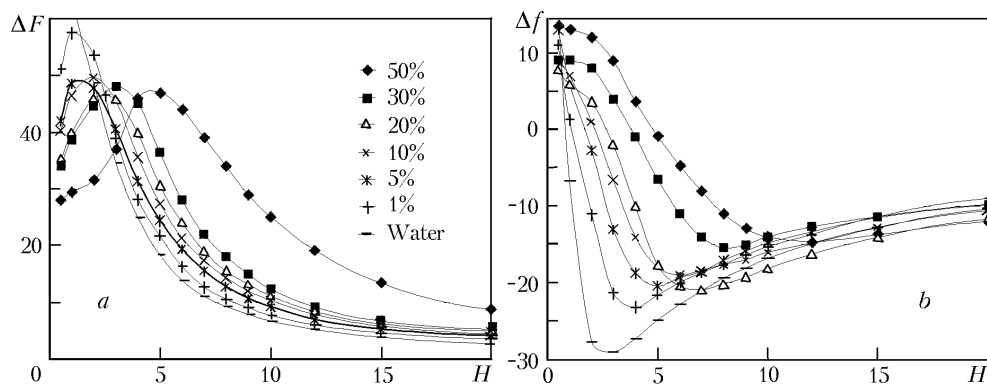
209

Fig. 6. Parameters of the relative broadening ΔF of the resonant curve (a) and the shift Δf of the resonant frequency (b) vs. thickness of the layer of the aqueous solution of glycerin. Δf and ΔF, Hz; H, μm.
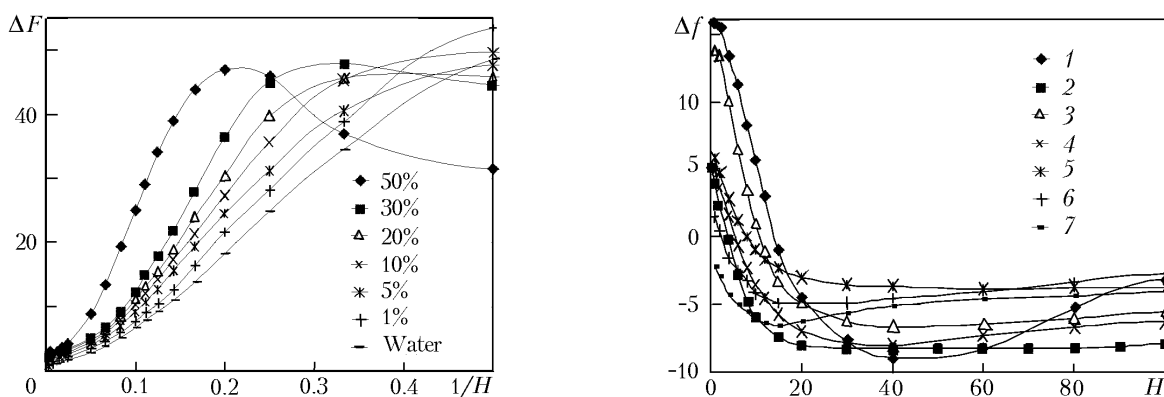

Fig. 7. Parameter of the resonant curve ΔF vs. inverse thickness of the layer of the aqueous solution of glycerin. ΔF, Hz; $1/H$, μm^{-1}.

Fig. 8. Shift of the resonant frequency Δf of piezoquartz vs. thickness of the layer of motor oils: 1–7) oils of different manufacturers; correspond to the notation of Table 2. Δf, Hz; H, μm.

higher, the higher the glycerin concentration in water. As the liquid-film thickness decreases, the quantity ΔF grows, attaining its maximum for a certain small layer thickness dependent on the concentration of glycerin.

It has been noticed that, as the percentage of glycerin increases, the ΔF maximum shifts toward larger thicknesses. As the film thickness decreases further, we observe a decreases in ΔF, which is attributable only to the structural change in the liquid layer. This change occurs under the influence of the solid quarts surface. Moreover, the liquid layers begin to show elastic properties for small thicknesses and possess shear elasticity, since Δf values have a minimum and begin to grow (Fig. 7).

The water layer in the gap between quartz surfaces, when its width is less than 2 μm, has a structure possessing shear elasticity thus showing the properties of a solid. It is assumed that the polar parts of the water molecules on the solid surface are self-organized into an ordered structure whose properties are manifested for small thicknesses. With addition of glycerin, the Δf minimum is observed for larger thicknesses of the liquid layer. This is due to the fact that the glycerin molecules combine with part of the water molecules, forming complexes with a denser molecular packing. Consequently, the layer of the glycerin solution has shear elasticity, which is manifested for larger thicknesses.

A characteristic feature of mechanical devices is the necessity of lubricating the surfaces of moving parts the distances between which are measured in nanometers. The fluid is subjected to shear deformation. Experiments with instruments of measure of surfaces forces on model lubricants have made it possible to reveal new facts associated

TABLE 2. Coefficient of Viscosity and Shear Elasticity of Motor Oils at a Temperature of 20°C

No.	Type of oil	G, kPa	$\eta \cdot 10^{-3}$, Pa·sec ($\dot{\gamma} = 1130$ sec^{-1})
1	TNK Tu 38. 301-41-148. 15W40	593	6.31
2	Mannol Racing. 10W40	326	2.84
3	Brit. Petrol. 10W40	620	4.67
4	Visco 3000. 10W40	376	4.08
5	Mobil Sup. 10W40	320	2.61
6	Moligen. 5W50	244	3.9
7	Shell Helix Plus. 10W40	135	3.62

with the mechanisms of lubrication in nanogaps. For lubrication of moving surfaces at a high velocity of motion (γ^5, sec^{-1}) one uses non-Newtonian fluids. It has been found that the viscosity of lubricant films retained in nanogaps is an order of magnitude higher than the viscosity of the same lubricants in a macroscopic volume.

Our investigation of the viscoelastic properties of motor oils with change in the film thickness has shown a fairly large spread in data among manufacturers on both the coefficient of viscosity and the dynamic shear modulus (Table 2).

Figure 8 plots the shifts of the piezoquartz resonant frequency Δf as functions of the thickness of the layer of the motor oils under study. An analysis of the plots presented has made it possible to determine the maximum thickness of the layer of the motor oils under study, wich possesses shear elasticity; the thickness of such a layer is dependent on the type of oil, i.e., on the manufacturer.

The change in the mechanical parameters of the materials under study in polymerization of epoxy adhesive and fluids, measured by the dynamic quartz-resonator method, enables us to judge the modification of the structure of boundary layers as a function of the processes that may occur at the interphase boundary.

The structure of liquid molecules may be complicated by adding organic, inorganic, and biological nanostructural elements. The capabilities of such changes have not been investigated yet; experiments with high rates of deformation are required.

Investigation of the process of polymerization and the viscoelastic properties of liquids by the dynamic quartz-resonator method provides a possibility of using it for investigation of:

(1) the interfaces at a micrometer level (functioning of the interfaces and determination of the structure and mechanical properties of the interphase layer);

(2) the processes occurring in the formation of the boundaries of different materials.

NOTATION

A, piezoquartz-vibration amplitude; C, concentration; ΔF_0 and ΔF_{load}, bandwidth of the resonant curve of free and loaded piezoquartz respectively; Δf, elastic shear of the resonant frequency; f_0, linear frequency; G, shear elasticity; H, liquid-layer thickness; k_0, coefficient of elasticity of piezoquartz; k, coefficient of elasticity of the interphase layer; L, optical path length of the beams; M, piezoquartz mass; m, sample's mass; $n = 1, 2,$ and 3, order of the interference band; R, coefficient of resistance of the liquid layer; R_0, coefficient of resistance; S, contact area of the liquid; T, time; U, voltage; β_0, damping factor; β_{load}, damping factor of the resonant system; γ, shear deformation; σ, shear stress; ω, angular eigenfrequency of piezoquartz; ω_{load}, resonant angular frequency of the system. Subscript: load, loaded; 0, constant.

REFERENCES

1. S. S. Voyutskii, *A Course in Colloid Chemistry* [in Russian], Khimiya, Moscow (1964).
2. H. Sonntag and K. Strenge, *Koagulation und Stabilitat disperser Systeme* [Russian translation] Khimiya, Moscow (1973).
3. Yu. G. Frolov, *A Course in Colloid Chemistry. Surface Phenomena and Disperse Systems* [in Russian], Khimiya, Moscow (1988).

4. M. C. Rocco, R. S. Williams, and P. Alivisatos (Eds.), *Nanotechnology in the Recent Decade. Prognosis of the Trend of Investigation* [Russian translation], Mir, Moscow (2002).

5. V. Yu. Naumenko, A nondestructive method of measuring the mechanical parameters of the border layers of polymers, *Kauchuk Rezina*, No. 1, 33–36 (2004).

6. V. Yu. Naumenko, On the mechanism of losses in the border layers of polymers, *Kompozit. Polimer. Mater.*, Issue 4, 21–24, Kiev (1979).

7. V. Yu. Naumenko and N. N. Firsov, Possibilities of application of the dynamic method for estimating the viscoelastic parameters of disperse media, in: *Ext. Abstracts of Papers presented at 22nd Symposium on Rheology*, 21–26 June 2004, Valdai (2004), p. 89.

8. E. V. Evstigneeva, V. Yu. Naumenko, V. V. Lavrent'ev, and I. A. Tutorskii, Investigation of the mechanical properties of the surface layers of the SBS butanedionestirole triblock-copolymers, *Vysokomol. Soedin. B*, **23**, No. 9, 650–653 (1981).

9. V. Yu. Naumenko and N. A. Konstantinova, Determination of the viscoelastic properties of cryoglobulines by the dynamic method of quartz resonator, *Med. Fiz.*, No. 10, 74–78 (2001).

10. V. Yu. Naumenko, Molecular-kinetic theory of formation of the molecular contact between a polymer and a solid body, *Kauchuk Rezina*, No. 3, 4–6 (2003).

11. S. P. Strelkov, *Mechanics* [in Russian], Nauka, Moscow (1975).