

RHEOLOGICAL PROPERTIES OF MINERAL OIL WITH HYDROGENATED  
BUTADIENE-STYRENE COPOLYMER

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It is known that motor oils with polymeric additives behave like Newtonian liquids. The rather sparse information available on their rheological properties pertains mainly to oils compounded with polyisobutylenes or polyalkylmethacrylates [1, 2]; no information is available on oils containing butadiene-styrene copolymers. Since the rate of shear in some components of engines may vary over extremely broad limits and may reach values as high as  $10^6 \text{ sec}^{-1}$  [1], it is extremely important to have an idea of how this factor will affect the viscosity of polymer-compounded motor oils.

In this article we will present data on the temperature dependence of rheological properties of oils compounded with a hydrogenated butadiene-styrene copolymer, over a wide range of rates of shear. We performed these studies on a polymer-compounded oil of the SAE 20W/40 class and an SK-1 lube base stock (BDS 9784-79) with a viscosity of  $6.68 \text{ mm}^2/\text{sec}$  at  $100^\circ\text{C}$ . The compounded oil was prepared from the base stock by adding 2% of a hydrogenated butadiene-styrene copolymer with a viscosity-average molecular weight of 90,000.

Since the rheological studies were performed over a broad range of shear rate gradients (from  $0.4$  to  $10^5 \text{ sec}^{-1}$ ) and an extremely broad range of temperatures (from  $-10^\circ$  to  $+100^\circ\text{C}$ ), over which the viscosity of the system changes by several orders of magnitude, we used the following instruments for the measurements: a Ubbelohde-type capillary viscometer, a Rheotest-2 rotating viscometer, and a capillary rheoviscometer (or high rates of shear). The copper capillary used in the rheoviscometer had a diameter of  $0.17 \text{ mm}$ , with a ratio of 100 between the length and radius.

Flow curves of the oil compounded with the hydrogenated butadiene-styrene copolymer, obtained at various temperatures, show the following: At temperatures below  $0^\circ\text{C}$  (Fig. 1b), these curves consist of three sections corresponding to flow of liquids with maximum and minimum Newtonian viscosity in the region of low and high shear rate gradients, and flow with a variable effective viscosity. The maximum viscosity reflects the behavior of a system with unbroken structure at low shear rate gradients, the minimum viscosity reflects the displacement of elements of structure that are maximally deformed under the influence of the deformation gradient; the effective viscosity reflects processes of deformation of structure and orientation of elements of the deformed structure. Under the influence of stress, the conformational globules of the polymer are oriented in the flow; and as a consequence, the viscosity of the system is reduced. The variation of viscosity at a given temperature but with different shear rate gradients is related to the relaxation nature of the deformation of the polymer chain.

A question arises: Is the decrease in viscosity of the solution of polymer in oil actually due to the increase in shear rate gradient, or might it be due to an increase in temperature? In a test using a copper-constantan thermocouple with an accuracy of  $0.1^\circ\text{C}$ , it was established that the efflux temperature of this solution remains unchanged. With the temperature constant, a proportional relationship was established between the shear rate gradient and the time for efflux of a given quantity of the oil base stock over a range of shear rate gradients from  $0.4$  to  $10^5 \text{ sec}^{-1}$ ; this also indicates that the process is isothermal. With increasing temperature, the difference between the maximum and minimum values of viscosity decreases (Fig. 1a); the minimum viscosity is reached at lower values of the shear rate gradient. This can be explained by the decrease in resistance of the liquid to flow.

It is interesting to follow the variation of the ratio of maximum and minimum viscosities as a function of temperature. This ratio decreases from 2.34 at  $-5^\circ\text{C}$  to 1.08 at  $100^\circ\text{C}$  (Fig. 2).

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VTU "A. K'nchev" (Ruse, Bulgaria). VKhTI (Sofia, Bulgaria). Translated from Khimiya i Tekhnologiya Topliv i Masel, No. 10, pp. 35-36, October, 1985.

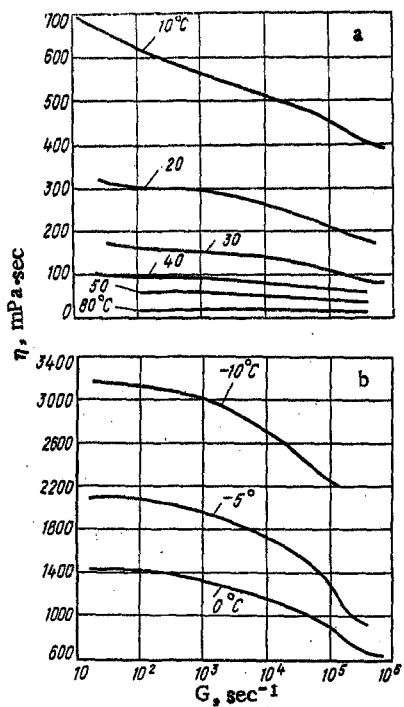


Fig. 1. Viscosity  $\eta$  as a function of shear rate gradient  $G$  for SK-2 oil compounded with 2% hydrogenated polybutadiene-styrene copolymer, at subfreezing temperatures (a) and above-freezing temperatures (b) (temperatures indicated on curves).

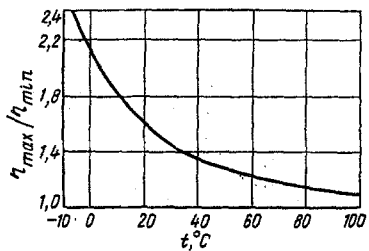


Fig. 2

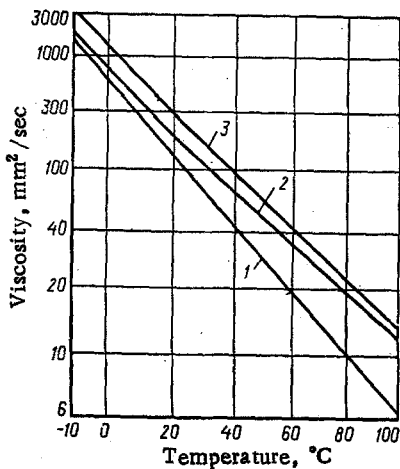


Fig. 3

Fig. 2 Ratio of maximum and minimum viscosities as a function of temperature  $t$  for SK-1 oil compounded with 2% hydrogenated polybutadiene-styrene copolymer.

Fig. 3. Viscosity-temperature relationship for SK-1 oil: 1) base stock; 2) compounded (minimum viscosity); 3) compounded (maximum viscosity).

At temperatures above 100°C, the ratio of the maximum and minimum viscosities is close to unity, and the difference between them is within the limits of error of measurement ( $\pm 5\%$ ).

In Fig. 3 we have plotted the maximum viscosity (curve 3) and the minimum viscosity (curve 2) on a Walther nomogram; we observe a change in the slope in the 20-40°C region, which has also been noted for oils compounded with other V. I. improvers [3]. At lower

temperatures, the viscosity most likely corresponds to a higher degree of association of the macromolecules in the oil; at higher temperatures, the associates are partly broken up. At temperatures below 0°C, the minimum viscosity is close to the viscosity of the oil base stock (Fig. 3, curve 1).

Thus, in the region of shear rate gradients from 0.4 to  $10^5 \text{ sec}^{-1}$  for a 20W/40 oil formulated with hydrogenated polybutadiene-styrene copolymer in the temperature interval from -10° to 100°C, we have established a decrease in the ratio of maximum and minimum viscosities as the temperature is increased. As a result, favorable conditions are ensured for the operation of internal combustion engines over the entire range of operating temperatures.

#### LITERATURE CITED

1. W. J. Bartz, *Mineraloeltechnik*, 19, No. 7, 19-27 (1974).
2. K. Kichke, *Colloq. Int. C.N.R.S. (Paris)*, No. 233 (Polymers and Lubrication), p. 136 (1975).
3. N. Drenchev, *Khim. Ind. (Sofia)*, No. 2, 67 (1977).