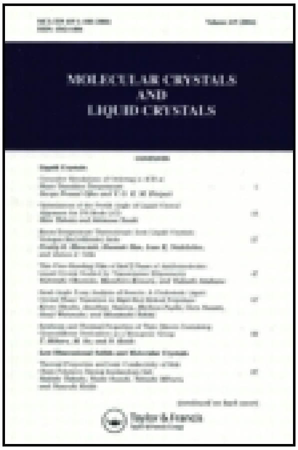

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006

To cite this article: Rudolf Eidenschink, Georg Konrath, Holger Kretzschmann & Michael Rombach (1999): Unusual Lift by Shearing Mesogenic Fluids, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 330:1, 327-334

To link to this article: http://dx.doi.org/10.1080/10587259908025606

Mol. Cryst. Liq. Cryst., 1999, Vol. 330, pp. 327-334
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Printed in Malaysia

Unusual Lift by Shearing Mesogenic Fluids

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The compounds hexakis- and pentakis[octylthio]benzene showing discotic phases below room temperature were sheared in an oscillation mode under load between a cylinder and a disk of chromium steel at temperatures between 60 and 120°C. Surprisingly, after some initial wear friction coefficients f decreased to values between 0.005 and 0.001. Under these conditions known lubrication oils cause boundary friction with values some 100 times higher. The nonmesogenic compounds hexakis[2-ethylhexylthio]benzene and hexakis[2-octylthio]benzene behave like known oils. Possible reasons for this promising behaviour of the mesogenic compounds are discussed.

Keywords: discogenic liquids; lubrication; phase transition; shear; tribology

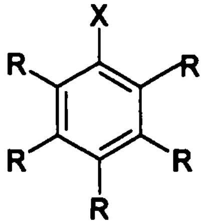
INTRODUCTION

The possibility of exploiting the anisotropy of viscosity of liquid crystal phases to improve sliding properties in bearings being operated in their hydrodynamic regimes has been discussed for almost 20 years[1]. The concept of using isotropic liquids formed by rod-like or disk-like molecules[2] as „intelligent lubricants" has reached applicability in real engineering[3]. In this situation molecular ordering is induced by pressure and/or shear. Discogenic liquids are of great interest because of their special tribologic effects and the economic aspect due to their relatively easy availability. Of particular importance is their behaviour in slide bearings that are operated in the regimes of boundary and mixed friction characterised by high energy losses and wear when known oils are used. Here, the results obtained under such practical conditions for two discogenic n-alkylarylsulfides and for two nonmesogenic alkylarylsulfides with branched alkyl chains are presented.

EXPERIMENTAL

Materials

The alkylarylsulfides 1 to 4 (Table 1) were prepared by nucleophilic substitution of the according halogen arenes with sodium alkylthiolates after known methods[4,5]. The purity of ≥ 99 per cent found by HPLC must be questioned because FD-mass-spectroscopy showed the presence of a few per cent of compounds with one substituent R being replaced by -H or -SH in the according formula.



Compound	R	X	Transitions	Viscosity mm²/s
1	$-SC_8H_{17}$	R	Cr 6°C I discotic below -10°C[6]	52
2	$-SC_8H_{17}$	H	Cr 12°C I discotic below 10°C	80
3	$-SCH_2CH(C_2H_5)C_4H_9$	R	no mesophase above -30°C	129
4	$-SCH(CH_3)C_6H_{13}$	R	no mesophase above -30°C	98

TABLE 1 Transition temperatures and kinematic viscosities at 40°C of compounds 1 to 4 (Cr = crystal, I = isotropic)

Method of measurement

Friction coefficients f were measured with a commercially available SRV rig[7]. A cylinder (100Cr steel, diameter 15 mm, length 22 mm) fixed in a holder and placed in a temperature-controlled chamber was rubbed under a preset load on a disk (100Cr steel, diameter 24 mm, height 7,9 mm) in a direction 10° (fixed by construction) from parallel to the long axis of the cylinder (Fig. 1): Here, all measurements were conducted with a load F_L of 50 N, a frequency of 50 Hz and a stroke length of 1 mm. The friction force F_F was measured by piezoelectric elements. f was calculated as F_F/F_L and monitored continuously. A few drops of the lubricating fluid were applied at the start. To avoid disturbances at the very beginning of the measurement by wear particles, a short run-in time (a few minutes) at reduced load is generally mandatory.

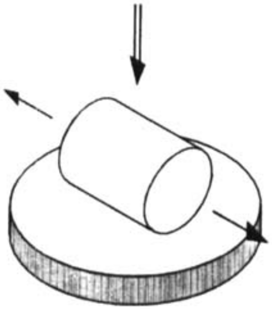


FIGURE 1
Direction of rubbing cylinder on disk (←→)
direction of load (⇓)

The roughness average R_a of the specimens was examined by a commercial laser profilometer[8] (spot size 1 µm, vertical resolution 10 nm).

RESULTS

Curve a in Fig. 2 shows the course of f in an SRV run with a standard lubrication oil at 120°C. Although the surfaces of the steel specimens are liable to wear, f-values of some 0.2 are accomplished without any shift to higher friction states by so-called surface seizure. Under the same conditions the discogenic compound 1 behaves in an unprecedented and reproducible way in that f declines to a stable level at 0.005. This level of f is only known from fast and uniformly moving slide bearings in their hydrodynamic regime and was never observed in a SRV rig. The time after which this bottom line is reached has a deviation in the order of 1 h and tends to increase with decreasing temperature. With 1 at 60°C and under else identical conditions the basis line of 0.003 was reached after 17 h.

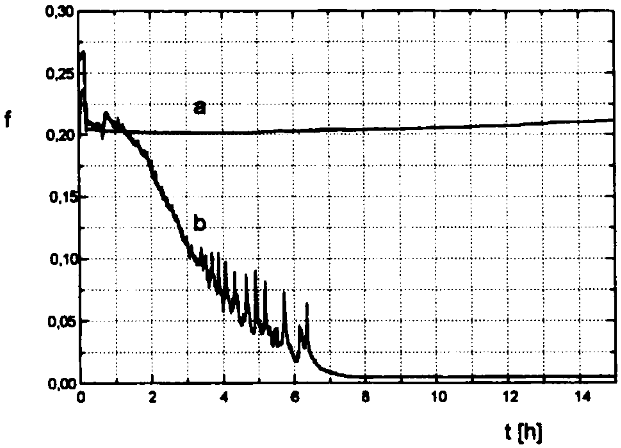


FIGURE 2 Friction coefficient f versus time t, cylinder/disk at 120°C, load 50 N, frequency 50 Hz, amplitude 1 mm, run-in time 600 s with 10 to 20 N, a standard lubrication mineral oil, viscosity 46 mm^2/s (40°C), b compound 1.

The region of decaying f is associated with an increase of the initial contact area of 0.5 mm^2 (calculated after Hertz) to some 4 mm^2 at 60°C (measurement of the scar area on the cylinder at the end of the run). The contact area at which the practically wearless „hydrodynamic" behaviour is observed also tends to increase with temperature (observation at 80, 100 and 120°C). Here we conclude that this behaviour is bound up with the enlargement of the contact area of the friction zone by temperature dependent wear in the initially valid modes of boundary and mixed friction and an attendant reduction of the pressure under constant load.

The contact zone of the rig can be regarded as sufficiently supplied by the fluids. Rewetting in the low friction state causes a temporary increase of f, presumably because fine metal particles are rinsed into this zone.

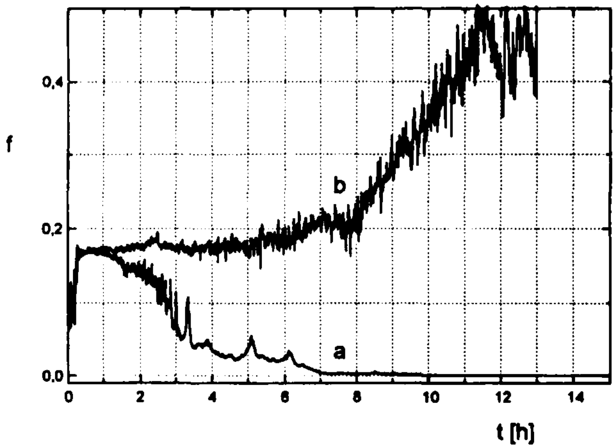


FIGURE 3 f versus t, cylinder/disk at 80°C, 50 N, 50 Hz, amplitude 1 mm, run-in time 300 s with 20 to 40 N, **a** compound 2, **b** compound 3.

Compound 2 shows a similar behaviour (curve **a** in Fig. 3). At 80°C an even lower level for f (some 0.001) is reached. The nonmesogenic compounds 3 and 4 did not show a decrease of f as exemplified by compound 3 at 80°C (curve **b** in Fig. 3). Moreover, both nonmesogenic compounds being isomers of 1 exhibited very poor wear protecting properties indicated by the increase of f which led to the automatic cut-off of the test runs. This result also demonstrates that a formation of a layer of metal sulfides during the friction process cannot contribute essentially to the low coefficients f found for 1 and 2.

The profiles of the scares on the cylinders and disks taken off in the „hydrodynamic" regime of the SRV-measurements were examined by a laser profilometer. Fig. 4 shows a typical profile orthogonal and Fig. 5 one parallel to the direction of oscillation. The composite roughnesses R_a are 0.14 µm, 0,11 µm, respectively. There are no significant differences in the roughness average at the end of the process when polished (starting with $R_a = 0.015$) or untreated specimens (starting with $R_a = 0.17$) are used.

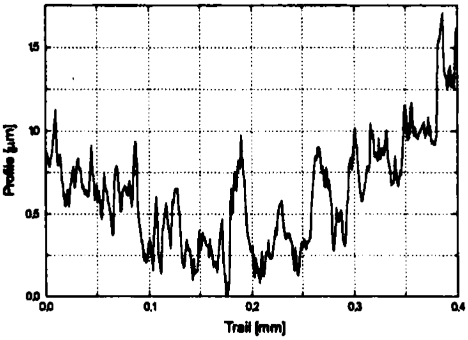


FIGURE 4 Surface roughness in a scar of a steel disk in the „hydrodynamic" regime at 60°C measured by a laser profilometer orthogonal to the direction of oscillation, R_a = 0.14 µm

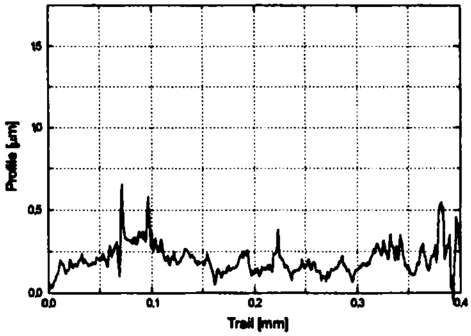


FIGURE 5 Surface roughness in the scar of Fig. 4, parallel to the direction of oscillation, R_a = 0.11 µm

DISCUSSION

The very low friction coefficients measured in the SRV rig with the mesogenic n-alkylarylsulfides <u>1</u> and <u>2</u> in slide bearings so far only reported from uniformly moving slide bearings operated with isotropic fluids in the hydrodynamic regime. A prerequisite for this to occur is that at a high sliding speed the pressure (a lift) derivable from Reynolds's equation compensates the load acting onto the contact area. The speed at which the transition from mixed friction to a continuous film without any contact between the asperities on the surfaces takes place is generally known to be proportional to load and reciprocally proportional to viscosity for a given geometry of a bearing [9]. Most authors consider that this transition occurs when the film thickness is about 3 times the composite roughness[10], here being some 0.7 μm. It is suggested to assign the observed effect to an additional lift the origin of which may lie in the mesogenic nature of these compounds.

The links between the practically exploitable effect and phase behaviour or even molecular aspects are not evident. Landau-de Gennes theory provides an explanation for the reduction of friction[11] when a presmectic lubricant is sheared under boundary conditions[12]. However, apart from a small temperature region close to the clearing temperature any smectic elastic forces leading to a separation of the sliding parts can only be relevant for a relatively small correlation length in the order of a few multiples of the molecular length. As mentioned above the film thickness expected to be of the order of an micron. Moreover, because the movement of the rig has also a small transverse component the assumption of grooves fitted to the longitudinal oscillation on the scale of a few molecular lengths seems to be unlikely. Also the possibility of formation of tiny contacts between asperities under micro-elastohydrodynamic conditions[10] does not allow for the extremely low values of f. The difference of at least 130°C between a possible phase transition and the temperature of operation at 10 MPa pressure observed in the case of $\underline{1}$ constitutes another obstacle. One of us (R.E.) sees this phenomenon in the context of the hypothetical principle of maximum energy flow[13]: the generation of surfaces by shear within the friction layer causes - in analogy to Poynting's theorem - an „exchange pressure" which like a static pressure can induce a molecular order being responsible for the lift. Such a lift being grossly constant if a phase transition was involved would fit into the findings that under very high hertzian pressure as predominant in bearings with point contacts only little influence of the mesogenic properties could be found so far. Another hint that there might be critical conditions for this lift to occur comes from precision measurements[14] of f in a *uniformly* moving slide bearing (steel/steel) at a very low load pressure of 0.02 MPa and low speeds at room temperature. The curves f versus G (dimensionless Gümbel's number representing angular speed x dynamic viscosity / load pressure) showed almost identical minima at the transition from mixed to hydrodynamic friction for $\underline{1}$ ($f_{min}3.1 \cdot 10^{-3}$, $G_{min}1{,}8 \cdot 10^{-3}$) and the oil of Fig. 2, curve **a** ($3.5 \cdot 10^{-3}$, $1{,}7 \cdot 10^{-3}$).

OUTLOOK

To obtain a better basis for understanding the effect of the „liquid crystal lift“ the molecular order in a uniform friction film between smooth surfaces should be made optically detectable. Also the dependence of f on the *self adjusting* layer thickness at different loads, speeds and temperatures must be clarified. This would help to find new and effective mesogenic lubricants which may solve a variety of problems bound up with friction and wear in engines.

Acknowledgements
We would like to thank Bernhard Schönauer (Institut für Verbundwerkstoffe, Kaiserslautern) for his hints to an unusual behaviour of discogenic lubrication oils in slide bearings and Matthias Hampel (Institut für Mikrotechnik, Mainz) for the laser profilograms.

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