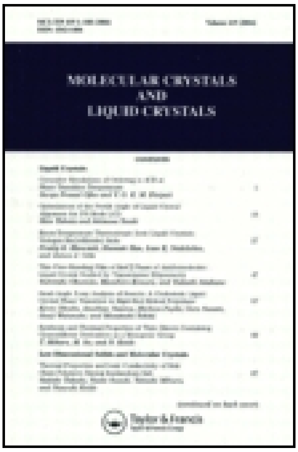

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The Estimation of Abilities of Liquid-Crystalline Compounds Dissolved in Paraffin Oil for Accumulation on Solid Surface

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The mixtures of two liquid crystalline compounds (6CHBT and 6CB) with paraffin oil of different concentration were tested as lubricating agents. A great decrease of friction coefficient was observed after doping the paraffin oil with liquid crystalline compounds, specially for higher loads (40, 50 N). The compound with cyano group 6CN gives better improvement of lubricating properties. The FT-IR measurements of tested mixtures shown the tendency of liquid crystalline molecules to accumulate on the metal surface.

Keywords Antiwear additives; friction coefficient; FT-IR; liquid crystals; surface accumulation

1. Introduction

Liquid-crystalline compounds added to typical lubricants improve their tribological properties [1–4]. Their quantity enough to improve tribological properties is usually not large (maximum several percent); according to Yao [1] even 1% of liquid crystalline compound is enough. This amount of the additive is not sufficient to create the liquid crystalline phase in the whole volume of lubricant. So the reason of improvement of tribological properties can be the creation of liquid-crystalline layer on the solid surface (metal). In many papers this suggestion can be found. Yao [1] shown that liquid crystalline compound 5CB dissolved in n-hexane, during the friction, adsorbs and orients on the tested surface. The layer of liquid crystalline compound causes the orientation of oil molecules, which leads to the formation of protecting layer decreasing the resistance movement during friction. Also from the theoretical work of de Gennes [4] or Sullivan and Shalaginov [5] it may be conclude that the compounds with a rigid structure and asymmetrical shape, showing nematic liquid crystalline properties or even not, can form close to metal surface smectic layer

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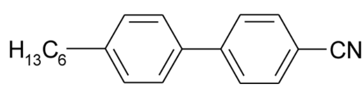
(presmectic phase) of the thickness of few molecules. The layer of liquid crystalline compound formed on the metal surface can be the additional protection and the reason of the improvement of tribological properties.

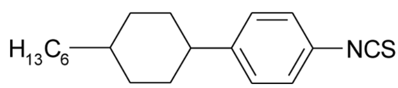
The aim of this work was to compare the abilities of two liquid crystalline compounds as additives to lubricant agent for improvement of tribological properties and to give the next evidence of the possibility of liquid crystalline compounds dissolved in paraffin oil to migrate from the volume of the lubricating mixture to the solid surface.

2. Experimental Methods

Two nematic compounds, 6CB and 6CHBT, of the following formulae:



nematic phase in the range 14.5°C–29°C



nematic phase in the range 12.5°C–43°C
were chosen as additives to paraffin oil. They were differing in the structure of rigid core and in the polarity of terminal group (-CN group in compound 6CB and –NCS group in compound 6CHBT). The compounds were added to paraffin oil in the following quantity order: 0.2, 0.5, 1 and 2 wt.%. They were dissolving completely forming clear liquid.

For mixtures of the composition 0.5, 1 and 2 wt.% the measurements with the use of T-11 tribotester, produced by ITME in Radom, were performed.

For tribological measurements the100Cr6 steel samples were used. Ball of the diameter equal to 0.5”, roughness $R_a = 0.032\,\mu m$ and hardness 60–65 HRC was used as a sample. The disc of the diameter equal to 25 mm, surface roughness $R_a = 0.175\,\mu m$ and hardness 45 HRC was used as a counter-sample. The samples were made according to the requirements of tribotester T-11. Measurements were performed at ambient temperature. The value of friction force were measured and the friction coefficient was determined.

The measurements were carried on under the following conditions: applied load 20, 30, 40, 50 N, rubbing speed 0.1 m/s and test time 900 s. The measurements of friction force were performed continuously with frequency 1 s, directly with the use of tensometric sensor. The value of the friction coefficient was calculated dividing the value of the friction force, rescaled by operating program by the value of the load used.

For mixtures of the composition 0.2, 0.5, 1 and 2 wt.% the measurements with the use of infrared spectrophotometer with Fourier transform (FT-IR), BIO-RAD FTS-175C, were performed.

The samples of mixtures as well as pure components (liquid crystals and paraffin oil) were measured in transmission as well as reflection mode in the wavelength range of 4000–1000 cm^{-1}. In the former case between CaF_2 windows and in the latter case on the metal surface.

3. Results and Discussion

3.1. *Results of Wear Measurements*

The measurements of friction forces let to calculate the friction coefficient, which values are presented in Figure 1, for lubricating mixtures containing 0.5 wt.% (a), 1 wt.% (b), and 2 wt.% (c) of compounds 6CB and 6CHBT dissolved in paraffin oil.

Introduction of liquid crystalline 6CHBT containing terminal group –NCS to paraffin oil causes the improvement of lubricating properties only under higher load (40 N and 50 N). The influence of its concentration on the value of friction coefficient under lower load (20 N and 30 N) was very small. The lowest values of friction coefficient were observed for 0.5 and 1 wt.% of this compound in paraffin oil and under load 40 N ($\mu = 0.058$) and 50 N ($\mu = 0.073$). The influence of the concentration on friction coefficient is well visible in Figure 2.

In case of the use of 6CB with terminal group –CN the influence of the concentration on the reduction of friction coefficient was observed, Figure 2b. The increase of the concentration causes the decreases of the friction coefficient. Also the increase of the load causes the decreases of the friction coefficient for mixtures with compounds 6CB, especially for 30, 40, and 50 N loads. The lowest values of friction coefficient were found under 50 N load for the mixture containing 2 wt.% of 6CB ($\mu = 0.039$).

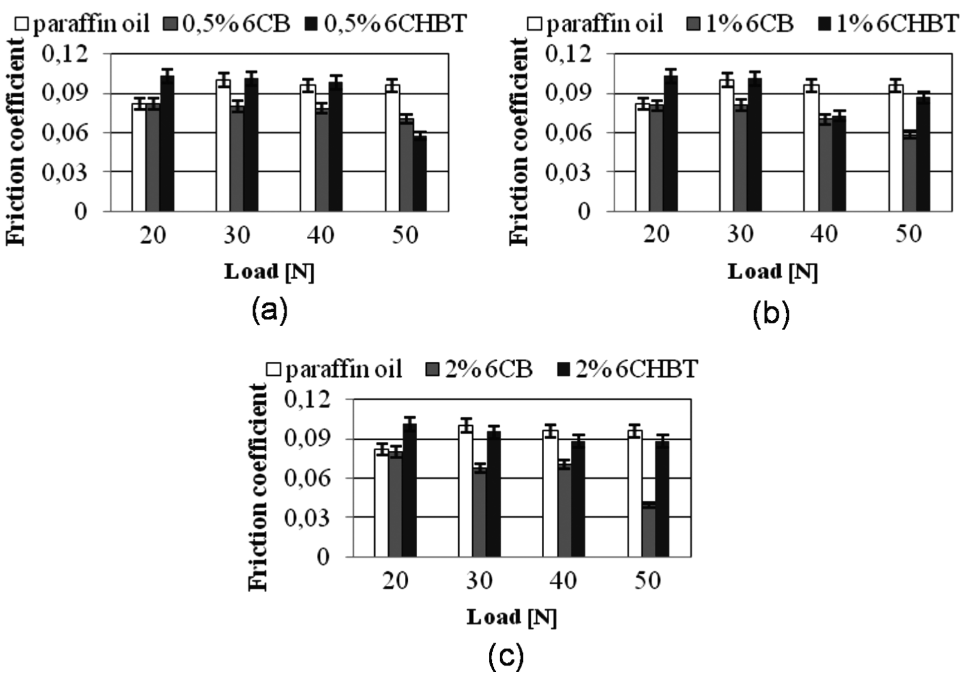


Figure 1. Friction coefficient for lubricating mixtures containing 0.5 wt.% (a), 1 wt.% (b), and 2 wt.% (c) of compounds 6CB and 6CHBT dissolved in paraffin oil.

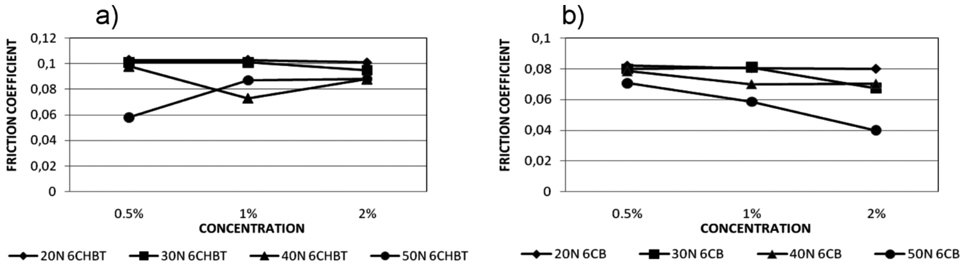


Figure 2. Concentration dependence of friction coefficient under different load (20, 30, 40 and 50 N) for lubricating mixtures of paraffin oil with compounds (a) 6CHBT and (b) 6CB.

It was found that the chemical structure, especially the type of terminal group, influences the tribological properties. Compounds with terminal group –CN decreased friction coefficient more than compounds with terminal group –NCS of the same amount.

3.2. *Results of FT-IR Measurements*

We have performed the FT-IR measurements in order to confirm the mechanism of the reduction of friction coefficient described in the literature [1,4,5].

3.2.1. *Transmission Mode.* The FT-IR measurements were performed for pure components (liquid crystals 6CHBT and 6CB as well as paraffin oil) to establish the wavelength range of absorption bands for each functional group.

The strongest and most characteristic absorption bands appear at 2039 cm^{-1} corresponding to stretching vibrations of isothiocyanato group –N=C=S (NCS) existing in compound 6CHBT and 2227 cm^{-1} corresponding to stretching vibrations of cyano group –CN existing in compound 6CB. These bands were taken into consideration in further experiment.

3.2.2. *Reflection Mode.*

Influence of the concentration. The spectra obtained for mixtures of 6CHBT and 6CB in paraffin oil in the concentration 0.2, 0.5, 1, and 2 wt.% measured in reflection mode are presented in Figure 3

The increase of the concentration of liquid crystalline compounds from 0.2 wt.% to 2 wt.% causes the increase of intensity of absorption peaks. It shows that the method used is proper for the quantity measurements of liquid crystalline compounds in paraffin oil.

Influence of the time after deposition. The idea of the first experiment which was undertaken to prove the migration of molecules of liquid crystalline compounds was to measure a few spectra of the same sample depositing on the metal surface in different time intervals.

The spectra for lubricant mixture containing 0.2 wt.% of 6CHBT were collected just after depositing the mixture on the metal surface (curve 1), and after 1 hour (curve 2), Figure 4. Despite very small concentration of the liquid crystalline compound the decrease of the intensity of absorption band corresponding to the stretching vibration of –NCS group was observed. It is due to the decrease of amount of

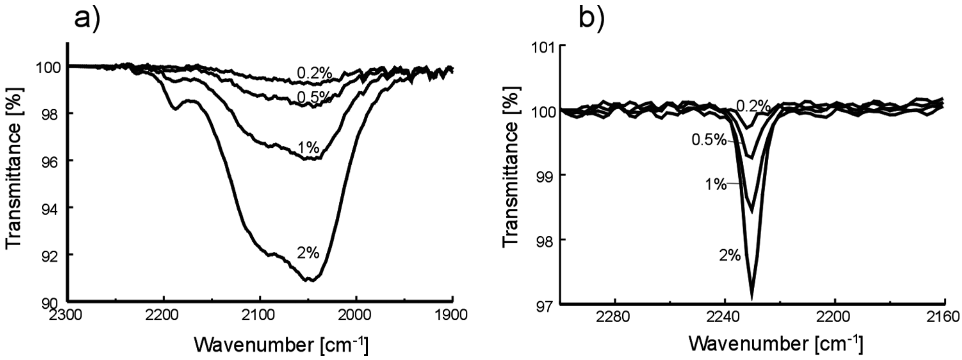


Figure 3. IR spectra of mixtures of paraffin oil with the (a) compound 6CHBT and (b) 6CB for the concentration 0.2, 0.5, 1 and 2 wt.% obtained in reflection mode (visible the range of absorption bands characteristic for terminal groups –NCS and –CN).

liquid crystalline compound on the free surface of the lubricant mixture, thus it has to migrate.

The idea of another experiment which was undertaken to prove that the liquid crystalline compound migrate from the bulk of the mixture was to collect the IR spectra of the same mixture differently treated before deposition on metal surface. The sample containing 2 wt.% 6CHBT in paraffin oil was measured after homogonous stirring and next day without additional stirring. The intensity of the absorption band corresponding to stretching vibration of –NCS group was higher in the case of the sample which was stirred (Fig. 5, curve 1). The lower intensity may suggest that in the sample that was not stirred the amount of 6CHBT is smaller in the volume of the sample thus it has to migrate, probably to the surface, in this case to the surface of glass bottle. The same may be in the sample measured 1 h after depositing (Fig. 4), the 6CHBT could migrate to metal surface and adsorb on it.

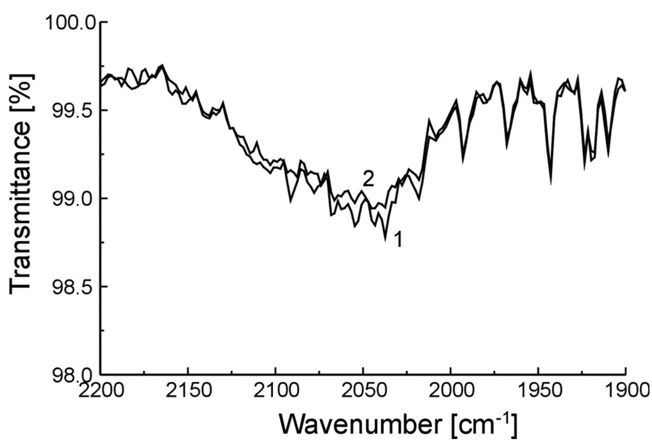


Figure 4. Absorption band of –NCS group for the mixture 0.2 wt.% of 6CHBT in paraffin oil curve 1 – after depositing the mixture on the metal surface, 2 – after 1 hour.

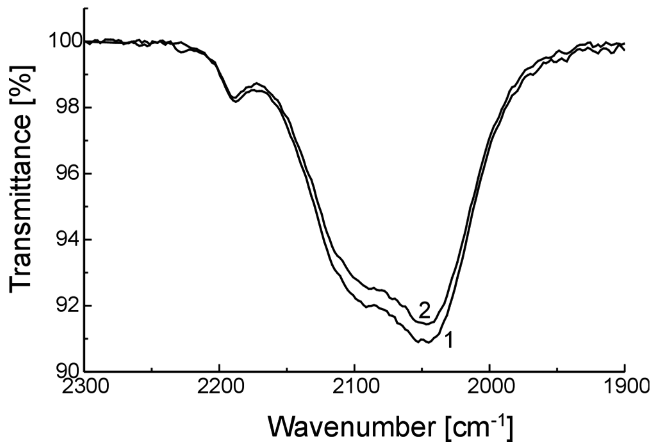


Figure 5. Absorption band of –NCS group for the mixture 2 wt.% of 6CHBT in paraffin oil: curve 1 – sample after stirring, curve 2 – without stirring.

4. Conclusions and Perspectives

The mixtures of liquid crystalline compounds 6CHBT and 6CN dissolved in paraffin oil used as lubricants have better tribological properties compared to pure paraffin oil. They decrease friction coefficient, especially for higher load. The molecular structure of two liquid crystalline components play an important role in this behavior. The compound with terminal cyano group 6CB cause bigger decrease of friction coefficient. This group is more polar than isothiocyanato group thus the molecules can easier accumulate on solid surface. The two experiments with IR spectrophotometer show that the concentration of liquid crystalline compound in the mixture in paraffin oil changes in the volume. It decreases in the layer close to free surface. We may conclude that there appears migration of the molecules towards the solid surface. Such conclusion is according to theoretical consideration about presmectic layers, which may be formed on the solid surface even when compound does not form liquid crystalline phase in the whole volume of the sample [4,5], and according to research of Yao [1] as well.

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