Tribological properties of paraffin oil doped with liquid crystalline mezogenes

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The paper presents description and analysis of the results obtained in the investigation performed on a disc-ball tribotester T-11. Samples of 100Cr6 steel were tested, while as lubricant the mixtures of paraffin oil, with addition of 0.5%, 1%, and 2% of liquid crystalline compounds, from two homologous series defined with nOBCAB and nCBB symbols, were used. The friction force and wear of a sample and a counter-sample were measured. The improvement in tribological and anti-wear properties was found for all mixtures in relation to paraffin oil. The best tribological properties and the best wearability were obtained for mixtures with a compound 8CBB. This compound differs from the others in formation of different liquid crystalline phases.

Keywords: thermotropic liquid crystals, lubricants, tribological characteristic, friction, wear.

1. Introduction

The wear of sliding metal pieces due to the friction is the main cause of taking a machine out of service. Oiling is the process counteracting unfavourable frictional phenomena. Mineral oils are generally used as a lubricating medium. The possibility of improvement in their lubricating properties is limited and that is why one must use dopants for the existing oils to improve them. Nowadays, the used additives for lubricating oils are among others graphite and molybdenum disulfide. A mechanism of lubricant acting with these additives is based on formation of the surface-active film filling irregularities of a material surface. These additives increase lubricity of the oil base because they possess the stronger ability of adsorbing oil than metal, and their layered structure enables formation of a slip plane. Liquid crystalline compounds, which are characterized by an oriented arrangement of molecules as well as a sort of positional ordering, can play the same role. Applications of liquid crystals, being in a pure state and additives for mineral oils, as lubricants have been reported in the literature in the last few years [1–4]. Liquid crystals due to the presence of polar groups (e.g. -CN) undergo the adsorption on the surface easily and can create well-ordered protecting layers on the surface of solid substances. However, the exact mechanism of action of these compounds is not well-known yet. It was showed in a course of the investigations and also guided by the authors of the present work that the essential unit influencing the improvement in tribological properties of liquid crystals is the structure and length of the rigid core of molecules [5]. Thus, the aim of this paper is to test tribological properties of the compounds having long rigid core, namely comprising three and four phenyl rings. Because the used compounds create liquid crystalline phases at higher temperatures, the investigation of their tribological properties was possible only for the mixtures with paraffin oil.

2. Liquid crystalline materials

The thermotropic liquid crystals having rod-like molecules with a terminal strong polar cyanogeno group -CN were chosen for investigations. Their structures, phase transition temperatures and the length of molecules calculated with the use of HyperChem program are as follows

\[ C_{12}H_{22} + nO \quad \text{COO} \quad \text{N=O} \quad \text{CN} \]

nOBCAB

6OBCAB Cr – 108°C – S_{Al} – 124°C – N – 277°C-Iso, \( l_{6OBCAB} = 2.97 \text{ nm} \)
7OBCAB Cr – 103°C – S_{Al} – 120°C – N – 269°C-Iso, \( l_{7OBCAB} = 3.06 \text{ nm} \)
8OBCAB Cr – 93°C – S_{Al} – 98°C – N – 259°C-Iso, \( l_{8OBCAB} = 3.21 \text{ nm} \)

\[ C_{23}H_{42} + i \quad \text{COO} \quad \text{N=O} \quad \text{CN} \]

nCBB

7CBB Cr – 123°C – S_{Al} – 136°C – N – 350°C – Iso, \( l_{7CBB} = 3.21 \text{ nm} \)
8CBB Cr – 118°C (monotropic transition S_{Al} – 108°C) – N_{lea} – 160°C – S_{Ad} – 298°C – N – 343 –Iso, \( l_{8CBB} = 3.25 \text{ nm} \)

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These compounds were synthesized at Prof. Dąbrowski laboratory of the Military University of Technology. They were used as additives to paraffin oil applied as a model oil base. The investigations of tribological properties were carried for 0.5 wt%, 1 wt%, and 2 wt% solutions of each liquid crystal in paraffin oil. The amount of liquid crystals in paraffin oil was chosen on the basis of Ref. 5, according to which the content of the liquid crystalline substance in the oil of above 2 wt.% does not improve tribological properties. The proper amount of the liquid crystal was added to the weighted out quantity of paraffin oil. The mixtures were heated to the temperature higher than the temperature at which the liquid crystalline compound melts. The received lubricate compositions were cooled after homogeneity to the room temperature.

3. Parameters of tribological process

For tribological measurements, the 100Cr6 steel samples were used. A 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 produced by ITME in Radom. Measurements were performed at an ambient temperature. The friction force value and wear of the counter-samples were measured and the friction coefficient was determined.

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

The degree of wear was established on the basis of microscopic measurements of longitudinal and transverse scars on the ball (sample) and on the basis of the weight loss of the counter-sample (disc).

SEM images of worn surfaces were obtained using Carl Zeis Jena (Germany) scanning microscope.

4. Results

The value of the friction coefficient for all studied lubricate mixtures, after several seconds was stabilized on the set level during the whole measurement, thus an average value from 900 measurements was taken into account. The results are shown in Fig. 1.

![Fig. 1. Dependence of a friction coefficient on the load for paraffin oil and its mixtures with liquid crystals in different concentrations.](image-url)
For all the tested mixtures of oil with a liquid crystal, decrease in the friction coefficient with respect to the pure paraffin oil was obtained. It is essential especially for the higher load of above 30 N. Especially significant decrease was observed under the load of 50 N for the mixtures with compounds of the series of nOBCAB for 1 wt.% of 7OBCAB and 0.5 wt.% of 8OBCAB. The influence of a concentration of liquid crystal compounds on the improvement in tribological properties was not found. One cannot also establish the influence of the length of an alkyl chain. The applied compound 7CBB, having different rigid core but similar molecular length ($l_{7CBB} = 3.21 \text{ nm}$) to the compound 8OBCAB ($l_{8OBCAB} = 3.21 \text{ nm}$) does not reduce the friction coefficient value.

However, a significant difference was observed in tribological properties for the compound 8CBB. The friction coefficients of the mixtures of this compound with the oil are much lower with respect to the paraffin oil as well as to the mixtures with other liquid crystalline compounds.

The molecules of the compound 8CBB are the longest. They have more rigid core (four phenyl rings and one linking group) than the compounds of nOBCAB series. The length of its core is also higher (2.01 nm) with respect to the length of a rigid core of the compounds nOBCAB (1.78 nm). On the other hand, the alkyl chain is also important. The change of the alkyl chain length from seven to eight carbon atoms in nCBB series causes significant change of the properties in a pure state. The long core and long tail cause that the compound 8CBB can form different liquid crystalline phases than the other tested compounds, namely $S_{Ad}$ and $N_{re}$. It suggests that the intermolecular interactions are different for this compound. Probably it is easier for molecules 8CBB to form arranged layers on the metal surface even for a small concentration of a compound in this region. Additionally, the preferred phase just after melting of a liquid crystalline compound is a nematic phase which favours the better filling of the surface.

Fig. 2. Length of wear scars of country-samples obtained after a friction process.
The wear of the friction pair, i.e., a sample-ball and a counter sample-disk was also studied applying the weight method, based on the comparison of the sample weight before and after the tribological test. The weight losses in all cases were very small, they were very often lower than the weight accuracy (0.0001 mg), the maximum weight loss of the disc was 0.0003 mg, i.e., on the edge of accuracy of the measurement. The values for paraffin oil were higher (from 0.0003–0.0006 mg). One can generally conclude that the wear of the friction pair with the use of the oil with liquid crystals was smaller than with the use of pure oil.

The length of wear scars obtained after the friction process were studied by SEM only for the mixtures containing a 1-wt.% addition of liquid crystals and the maximum load of 50 N. The investigation results are shown in Fig. 2.

One can conclude that the observed wear scars after the friction process are not large. No gaps in the material of a counter-sample were observed. The lowest wear was observed for the mixture containing 1 wt.% of 8CBB because the observed wear scar is very narrow and very bright (almost invisible), i.e., it is very shallow. Thus, the investigations of the wear of the disc after the friction process confirmed that the compound 8CBB used as the paraffin oil additive causes improvement in wearability.

5. Discussion and conclusions

The liquid crystalline compounds used as additives to paraffin oil show certain analogy to antiwear (AW) agents. The mechanism of acting of antiwear additives consists in formation of the layer of their molecules on the metal surface. The polar part of the molecule of AW additives is adsorbed by a metal surface and a hydrocarbon part is turned toward oil direction. As a consequence, the oil film arises separating the working parts of the friction pair which reduces the wear and decreases the wear coefficient. The use of a liquid crystal (with ordered molecules) as the oil additives causes additionally a suitable arrangement of the oil molecules and thus reduces the material wear and the wear coefficient effectively. It was showed in the course of our investigations that the best properties were obtained using the compound 8CBB which creates a nematic liquid crystal phase. The improvement in tribological properties was not observed for shorter analogue of the compound 8CBB, having seven carbon atoms in the alkyl chain (7CBB). The influence of the alkyl chain length for another homologous series (nOBCAB with n = 6, 7, or 8) was not also observed. The compound 8CBB differs from the other compounds in formation of different liquid crystalline phases.

References