THE TRIBOLOGICAL EFFECTIVENESS OF SOME 2-HYDROXYACIDS IN 1-METHYLNAPHTALENE WITHIN THE FRAMEWORK OF TRIBOPOLYCONDENSATION PROCESS AS A BOUNDARY LUBRICATION MECHANISM

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Abstract: *Tribopolycondensation process as a boundary lubrication mechanism is both very effective and extremely complex from the tribochemical point of view. The present study is aimed at a better understanding of the action mechanism of 2-hydroxyacids in 1-methylnaphtalene. The results obtained in the present paper proved that the tribopolycondensation mechanism for 2-hydroxyacids should be excluded and their wear reduction effectiveness controlled by a typical tribochemical reaction in which the carboxylic and hydroxyl groups play the major part.*

Key-words: tribopolycondensation, 2-hydroxyacids, boundary lubrication and 1-methylnaphtalene, tribochemistry.

1. Introduction

The demand for environmentally adapted lubricants is increasing. The importance of knowing more about the lubrication capabilities follows this need. Oxygen containing compounds have long been recognized and widely used as antifriction and anti-wear additives. Esters and polyesters are applied as synthetic base oils. The simplest tribological additives belonging to oxygenates have one polar group capable of adsorption at surface, for example, fatty acids and fatty alcohols. Aliphatic esters are used as base oils because they perform better than mineral oils. Usually esters have superior lubricity than mineral oils. More complex compounds have two oxygen containing polar groups. They can be similar, as diacids, diols, and diesters, or different as hydroxyacids and alkyl monoesters of diacids [1,2,3,4,5]. The most complex compounds include three or four oxygen containing polar groups. The best examples for this type of chemicals are (i) C_{36} dimeracid/diol monoester, (ii) trimethyllopropane esters, and (iii) pentaerythritol esters.

From the view-point of anti-wear properties, type (i) chemicals are the most effective anti-wear additives [6]. Usually, these additives relate to monoesters of the tribopolycondensation concept, introduced over 30 years ago by Furey [7]. This concept encompasses both tribopolycondensation and vinyl tribopolymerization. To describe these processes normally the term tribopolymerization is applied. The basic concept of tribopolymerization as a mechanism of boundary lubrication has been discussed in detail. tribopolymerization is defined as the planned or intentional formation of protective polymeric films directly and continuously on rubbing surfaces to reduce damage and wear by use of minor concentration of selected monomers capable of forming polymer film in situ (e.g. by polycondensation or addition processes). The results of high contact stress tribological tests using a ball-on-flat geometry demonstrated that the C_{36} dimer acid/ethylene glycol was extremely effective in reducing wear in both unidirectional and oscillating contact, clearly confirming the unusual effectiveness of this additive found for the first time by Furey [8].

The primary objective of this paper is to provide a more comprehensive comparison of the relative steel ball wear reduction capabilities from different compounds containing both carboxylic and hydroxyl groups under boundary lubrication conditions. Another objective of the present research is to find out the influence of the additive concentration in 1-metyhlpthalene. This also involves finding out the influence of alkyl chain length of 2-hydroxyacids on their anti-wear behavior.

2. Experimental Technique

2.1 Materials

Three different hydroxyacids, one carboxylic acid and one alcohol, were chosen as lubricity additives. Formulae and properties of these compounds are shown in Table 1. All compounds and 1-methylnaphthalene were purchased directly from the manufacturer and they were used without further purification.

The compounds were dissolved in 1-methylnaphtalene. The solutions: 0.01; 0.03; 0.05 and 0.1% (m/m).

Tabel 1. Formulae and properties of compounds used in the study.

Compound name	Abbreviation	Purity	Source of compounds
2-hydroxyoctadecanoic acid	HC18	≥ 97	sigma
2-hydroxyeicosanoic acid	HC20	≥ 97	sigma
2-hydroxydocosanoic acid	HC22	≥ 97	sigma
2-hydroxytetracosanoic acid	HC24	≥ 96	Fluka
Octadecanoic acid	Ac	≥ 96	Fluka
Octadecanol	Oh	≥ 96	Fluka

2.2 Apparatus and Test Conditions

T-01 pin-on-disc tester, manufactured by the Institute of Technology in Radom, Poland, was used to evaluate anti-wear and antifriction properties of the additives.

The pin-on disc test conditions were controlled to achieve boundary lubrication regime under 10N load. Before the test, both the ball and disc were washed with acetone in ultrasonic bath. After the test, wear scar diameters were measured and the volume of the wear was calculated.

Pin-on-disc test outputs: Wear-scar diameter was measured in both the *X* and *Y* directions using a photomicroscope to an accuracy of ±1 μm, and the *MWSD* was evaluated:

$$MWSD = (X + Y)/2$$

VW was calculated from the *MWSD* as follows:

$$VW = (2/3 * \pi * [(D/2)^3 - \sqrt{(D/2)^2 - (MWSD/2)^2} * ((D/2)^2 + 0.5 * (MWSD/2)^2)]$$

where *D* is the diameter of the test ball (*D* = 3.18 mm).

The relative wear (*RW*) was calculated as the ratio of the volume of ball wear obtained for the solution of additive in the 1-methylnaphthalene (*VW*add) and the volume of ball wear for the base fluid (*VW*b):

$$RW = (VWadd/VWb) \times 100\%$$

Table 2. Experimental set-up and test conditions.

Geometry	**Ball-on-Flat**
Specimens: Ball	3,18 mm diameter 63 HRC bearing steel R_a = 0,3-0,35
Disc	25,4 mm diameter; 75 HRC bearing steel; 7 mm thickness R_a = 0,5÷0,55 μm
Applied load	10 N
Wear track radius	8 mm
Sliding velocity	0,250 m/s
Sliding distance	500 m
Temperature	25 ^{0}C

2.3 Surface Analysis

To investigate the organic layer on the wear tracks, an i-series PE Fourier Transform Infrared Microspectrophotometer (FTIRM) was used. Reflection spectra were recorded in the range of 4000 to 700 cm^{-1} with a resolution of 4 cm^{-1} (100 scans at each point). All spectra were corrected by subtracting spurious bands originating from carbon dioxide, near 2350 cm^{-1}, as well as smoothing by the Savitsky-Golay method and multipoint normalization of the baseline. The mathematical processing of spectra shows no influence on their appearance.

3. Results and Discussion

The results of pin-on-disc for solutions of all the compounds in 4 different concentrations in 1-methylnaphthalene and 10N load are presented in Table 3. For each solution, five tests were carried out.

Table 3. Comparison of ball wear reduction of different additive concentrations in 1-methylnaphthalene under 10 N load.

Concentration [%] (w/w)	0.01	0.03	0.05	0.1
HC18	43 ± 4	55 ± 2	64 ± 3	75 ± 3
HC20	52 ± 7	63 ± 3	76 ± 4	83 ± 2
HC22	58 ± 6	72 ± 3	81 ± 2	90 ± 2
HC24	64 ± 4	76 ± 4	87 ± 3	92 ± 3
Ac	32 ± 8	40 ± 5	51 ± 6	59 ± 3
Oh	20 ± 6	33 ± 8	44 ± 4	48 ± 5

Figure 1 represents the concentration influence of the additives on their antiwear effectiveness. This figure clearly shows that the effectiveness of the all additives increases with the additive concentration increase. On the other hand, the 2-hydroxycarboxylic acids were more effective in wear reduction than octadecanoic acid and octadecanol. This could be indicated by the polarity of 2-hydroxycarboxylic acids, which is greater than this for octadecanoic acid and octadecanol. As shown in Figure 1, for 2-hydroxycarboxylic acids it was noted that their anti-wear properties increase with the increase in alkyl chain length. The results indicate that van der Waals force between alkyl chains of additives molecules to make oriented molecular layers seems to play an important role in the anti-wear property.

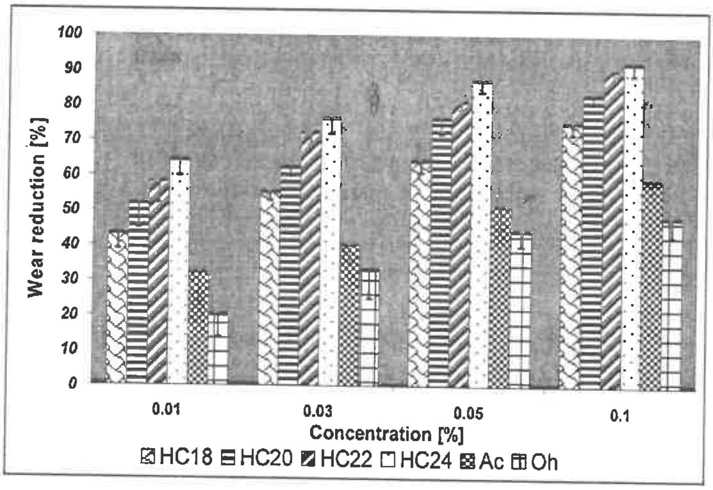

Fig. 1. The influence of additives concentration in 1-methylnaphthalene on the anti-wear effectiveness.

4. Tribochemical Reactions of 2-hydroxyacids with Steel Surface

To explain the tribochemical reaction mechanism of 2-hydroxyacids under boundary lubrication conditions, FTIR surface analysis after the friction process was used. The preliminary FTIR spectrum taken from the steel wear track lubricated with 0.1% (w/w) solution of HC22 in 1-methylnaphthalene is presented in figures 2 and 3 below.

The characteristic feature of spectrum on Figure 2 is an appearance of strong absorption bands at 1598 cm^{-1}, 1540 cm^{-1}. These peaks can be assigned to -C-O-Me group stretching in chelate compounds [9].

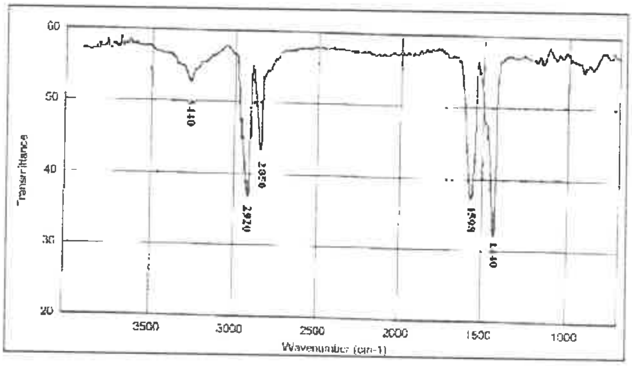

Fig.2. FTIR spectrum taken from the steel wear track lubricated with 0.1% (w/w) solution of HC22 in 1-methylnaphthalene.

Figure 3 presents FTIR spectrum taken from a different point on the same disc. It looks totally different from pervious spectra, which is normal in this case. It is worth mentioning that the presence of different products of tribochemical reactions on the wear track is noted, for example, for the tribochemical reactions of n-hexadecane and solutions of hexadecanoic acid [10].

The spectra on Figure 3 presents, a typical spectrum for the organometalic compound and the most important bands are:

- 1710 cm^{-1} – assigned to stretching group C=O,
- 1350 - 1330 cm^{-1} - assigned to stretching group C—O,
- 1450 - 1400 cm^{-1} - assigned to bending vibration of C—H in —O—C(=O)— CH_2— system.

The important finding here is that there was no evidence of polymeric film formation on the wear track, which should be companied with a band near 1740 cm^{-1}.

According to the tribopolicondensation mechanism, the FTIR spectra from different points of wear track lubricated with 2-hydroxyacids should be similar because of the polymeric protective film formation. Another argument which supports this finding is the fact that different 2-hydroxyacids have different effects in wear reduction, which according to the tribopolycondensation mechanism, should have similar effectiveness since they have the same capabilities for the formation of protective film.

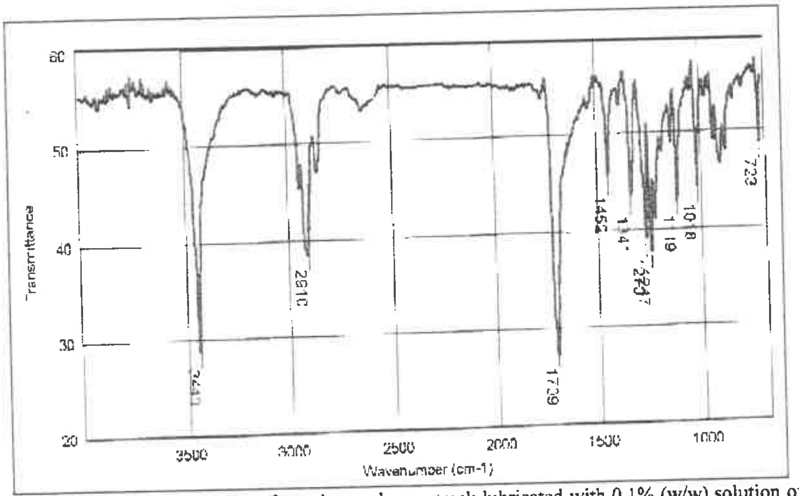

Fig. 3. FTIR spectrum taken from the steel wear track lubricated with 0.1% (w/w) solution of HC24 in 1-methylnaphthalene.

5. Conclusions

1. All the compounds investigated in the study were effective in wear reduction.
2. The effectiveness of 2-hydroxyacids increases with the increase in the alkyl chain length.
3. Tribopolycondensation mechanism for 2-hydroxyacids should be excluded. This conclusion is supported by the fact that:

   a. the FTIR spectra from different points on the same disk are different;
   b. the different 2-hydroxyacids have different effects in wear reduction; and
   c. surface analysis did not show any evidence for the formation of polymeric film since there was no band around 1740 cm^{-1}.

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