WEAR BEHAVIOUR AND TRIBOCHEMICAL REACTIONS OF LOW MOLECULAR DICARBOXYLIC ACID ESTERS UNDER BOUNDARY LUBRICATION OF THE STEEL-ON-STEEL MATING ELEMENTS.

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ABSTRACT:-

The action mechanism and the reactivity of some of dicarboxylic acids esters in sliding contacts of steel-steel surfaces which are used as synthetics base oil lubricants were investigated by tribological tests. Moreover antiwear properties of diester under boundary lubrication in steel-steel system have been studied. Surface analysis of products of chemical reaction has been investigated by using FTIR microscopy.
New absorption bands at 1716 cm^{-1} were found on steel substrate which belongs to organometalic compounds containing carbonyl group.

INTRODUCTION:-

Oxygen containing compounds have long been recognized and widely used as antifriction and antiwear additives [1,2]. The simplest tribological additives belonging to oxygenates have one polar group capable of adsorption at surface, for example, fatty acid and fatty alcohols. Antiwear reducing properties of these compounds have also been investigated and discussed in detail [3-7]. A typical example for that was fully described in [7] which presents tribochemical reactions of stearic acid on copper surfaces by using IR microscopy. More complex compounds have two oxygen containing polar groups. They can be similar, as in diacids, diols, and diesters, or different, as in the case of hydroxyacids and alkyl monoesters of diacids. Some of dicarboxylates were also used as antiwear additives for lubricating oils, such as monoesters of dicarboxylic acids and diols [8-10]. Their antiwear activity is related to the concept of *in situ* tribopolymerization as proposed by Furey [11-14]. According to this concept the additive molecules adsorbed on tribological surface are polymerizing directly on rubbing surfaces to form a thin protective film which reduces friction contact and wear.

The potential tribopolymerization and mechanism of monoester additives under fretting contact conditions have been also studied [15]. The tribochemical behaviour of several monomers were also investigated in both steel-on-steel and steel-on-aluminum systems. It was also found that the tribopolymerization did not occur in the metal system with C36 dimer acid partial esters under the fritting contact conditions used in the previous study [15]. Additionally it was emphasized that for condensation type monomers, the most important factor is the temperature of the rubbing surfaces. On the other hand, based on FTIR spectra findings described in

[16], it was shown that the mechanism of wear reduction of the monoester is the one involving a chemical reaction with substrate alumina followed by the formation of oligomer/polymer chain is complex, and other peaks in spectra have yet to be identified.
On the other hand, it was based on FTIR spectrum, which was described in [16]. The proposed mechanism of wear reduction of the monoester is that which involves a chemical reaction with alumina substrate followed by the formation of oligomer/ polymer chain complex. The present work relates wear behaviour of low molecular diesters and their tribochemistry to provide more information on and better understanding of the steel-on-steel wear process lubricated with these compounds. Therefore the present study includes the primary objective

(i) The influence of the diesters on the steel mating element wear.
(ii) To elucidate tribochemical reactions of diethyl succinate proceeding on the steel mating element under similar test conditions.

EXPERIMENTAL TECHNIQUE

Apparatus and lubricants

Tribological tests. To perform tribological tests under boundary lubrication conditions, a T-01pin-on-disc tester was used. Elements of the friction pair (balls and disks) were made from 52100 bearing steel, 63HRC, Ra = 0,5-0.55μm. Detailed description of both specimens is included in Table 1. The specimens were clamped in place with stainless steel holders. The lower holders contained the lubricant fully flooding the contact region. A dead- weight-loading system applied the normal force. Pure diesters were selected as lubricants for this research.

Material system		Steel-on-Steel
Geometry		Ball-on-Flat
Specimens:	Ball	3,18 mm diameter 63 HRC bearing steel
	Disc	25,4 mm diameter; 60-63 HRC bearing steel; 7 mm thickness R_a = 0,5-0.55 μm
Applied load		9.81N
Wear track radius		8 mm
Sliding velocity		0,250 m/s
Sliding distance		500 m
Environment		Ambient
Temperature		25 ^{0}C

Table 1. Experimental set – up and test conditions

Test conditions and the procedure

Eight aliphatic dicarboxylic esters were chosen as antiwear lubricants in this study. Formulas and properties of these compounds are shown in TABLE 2. Test conditions were designed to result in boundary lubrication at the sliding contact. All the tests were carried out under the same operating conditions. TABLE 1 also summarizes the test conditions used. Prior to use, the steel specimens were ultrasonically cleaned in acetone for 20 minutes. Minimum three tests were performed for each lubricant. All the diesters used in this study were obtained commercially in the highest purity available. The seals were cleaned before testing the next diester. The ball wear scar diameter was measured after unloading the specimens, using a photomicroscope.

Table 2. Characteristic of used compounds

Compound name	Used abbreviation	Molecular weight g/mol	Purity %	Source of the compound
Diethyl Malonate	**DEhMal**	160	98	Fluka
Diethyl Succinate	**DEhSuc**	174	99	Fluka
Diethyl Adipate	**DEhAdp**	202	99	Fluka
Diethyl Sebacate	**DEhSeb**	258	99	Fluka
Dibutyl Malonate	**DBuMal**	216	>98	Fluka
Dibutyl Succinate	**DBuSuc**	230	99	Fluka
Dibutyl Adipate	**DBuAdp**	258	>98	Fluka
Dibutyl Sebacate	**DBuSeb**	314	99	Fluka

Surface analysis

Products of chemical reactions present on the steel surface due to friction were identified by means of FTIR microscopy using Perkin-Elmer i-Series microspectrophotometer instrument. The spectrometer was operated in mid-infrared range (580-4000cm^{-1}) with 4cm^{-1} resolution and average signal over than 100 scans for background and disc. This technique allowed generation of spectra at any point of scanned surface. All obtained spectra were corrected by zapping of spurious bands which originated from carbon dioxide and water vapour, then each spectrum was smoothed by Savitsky–Golay method and multipoint normalizing of base line using Perkin-Elmer software GRAMS 2000.

Results and Discussion

The ball wear scar diameter results for steel lubricated with pure diesters are summarized in table (3), and illustrated in figures (1) and (2).

Table 3. **Comparison between the steel ball wear scar diameter lubricated by different diesters.**

Compound name	WSD mm*10^{-1}
Diethyl Malonate	4.821
Diethyl Succinate	4.632
Diethyl Adipate	3.734
Diethyl Sebacate	3.080
Dibutyl Malonate	3.562
Dibutyl Succinate	3.121
Dibutyl Adipate	3.011
Dibutyl Sebacate	2.460

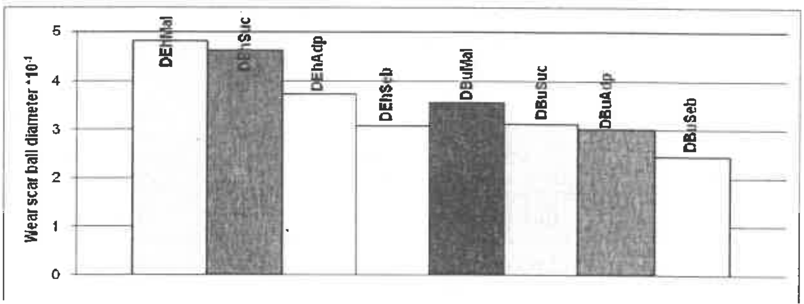


Fig. 1 Comparison between the steel ball wear scar diameter lubricated by different diesters.

The results presented in Figure (1) show the wear performance differences for the tested diesters. This figure clearly shows that, the ball wear scar diameter (WSD) decreases with increasing diacids alkyl chain length part of diesters. For example, the WSD in the system lubricated with DEhMal, DEhSeb are 4.821*10^{-1}mm, 3.080*10^{-1}mm, and with DBuMal, DBuSeb are 3.562 *10^{-1}mm 2.460 *10^{-1}mm respectively. On the other hand, increasing of alcohols alkyl chain length part of diesters results in reduction WSD. For example, the WSD in the system lubricated with DEhMal, DBuMal are 4.821 *10^{-1}mm and 3.562 *10^{-1}mm.

Based on these date, we can state that, WSD depend on the molecular weight of the diesters. Fig. (2) represent the relationships between the wear ball scar diameter (WSD) and molecular weight of the tested diesters. This figure clearly shows that, the WSD decreases with increasing molecular weight of diester. On the other hand, increasing the molecular weight of diester by increasing the diacid alkyl or by alcohol alkyl chain length of diester, gave the same almost effect antiwear properties. For example the diesters DEhSeb , DBuAdp which have the same molecular weight (258 g\mol) , the WSD lubricated with these diesters approximately equal 3.08 cm^{-1} and 3.11cm^{-1} respectively.

It can be concluded that the molecular weight value of the investigated diesters is a significant factor controlling the steel ball wear for metal/metal system lubricated with these diesters.

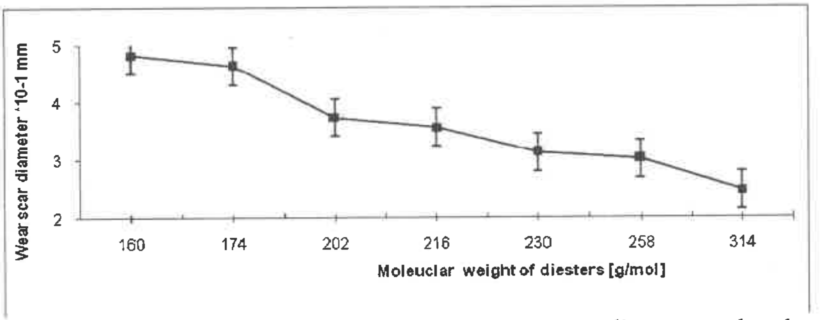


Fig.2 Relationships between the steel ball wear scar diameter and molecular weight of diesters.

Tribochemical reactions of diesters with steel surface.

FTIR surface analysis after the friction process was used to explain the tribochemical reaction mechanism of diesters in boundary lubrication conditions. FIG. (3) exemplify the preliminary FTIR spectrum taken from the steel wear track lubricated with pure diethyl succinate. Characteristic feature of this spectrum is the appearance strong absorption band at 1529 cm^{-1} this peak can assigned to -C-O- group stretching in chelate compounds, and 1716 cm^{-1} peak can assigned for C=O group diesters stretch [17].

The most specific situation arises from the fact that similar peaks were found in spectra taken from aluminum wear tracks lubricated by vinyl monomers [18] For example, the FTRIMA spectrum from the diallylphthalate wear products showed intense duplex peaks observed in the region of 1530 cm^{-1} to 1600 cm^{-1}. The spectrum also showed much- reduced peaks in the characteristic diallylphthalate absorption regions at 1725 cm^{-1} and 1280 cm^{-1} , related to the C=O and C-O-C stretching of the ester groups respectively. It is to emphasize that investigating the action mechanism of alcohols under boundary sliding conditions of an steel-on-steel system some similar peaks were observed [19], these absorption bands encompass mostly the region of 1522-1549 cm^{-1} , which usually is combined with the absorption bands around 1653-1680 cm^{-1}. They have been assigned to organometallic compounds including double bonding.

In the above discussions it may be said that ester groups present in a wide variety compounds do react with metals surfaces under boundary lubrication conditions, to great antiwear protective layers.

We propose that also in this case, the dominant formation process of reactive species forming the antiwear organometallic compound film on the steel friction tribological contact area, proceeds according to the anion redical action mechanism (NIRAM) approach. This approach (NIRAM) demonstrated that low energy electrons, which are spontaneously emitted from rubbing surfaces, can be the key factor in some tribochemical reactions, was formally postulated by Kajdas in relatively recent work

[20-22]. He proposed a concept of ionization of lubricant components by low-energy exoelectrons (1 to 4 eV), which are emitted from freshly formed surfaces in the friction of mating surfaces.

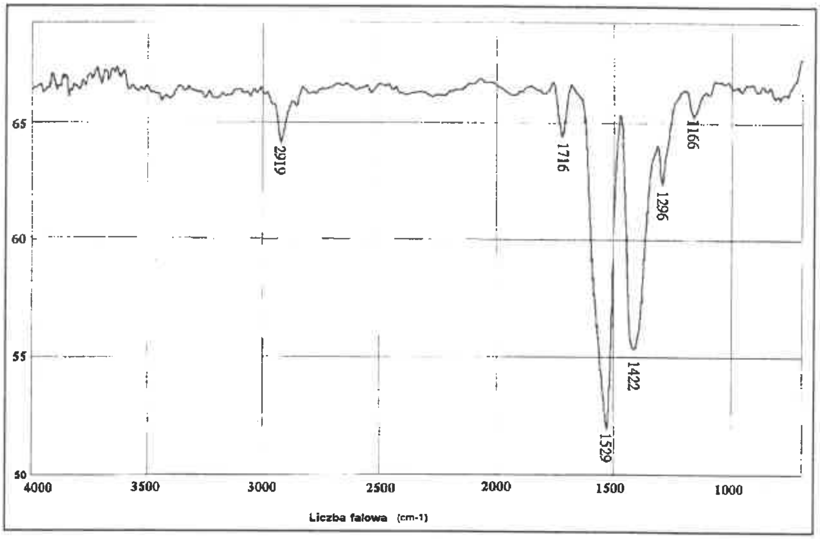
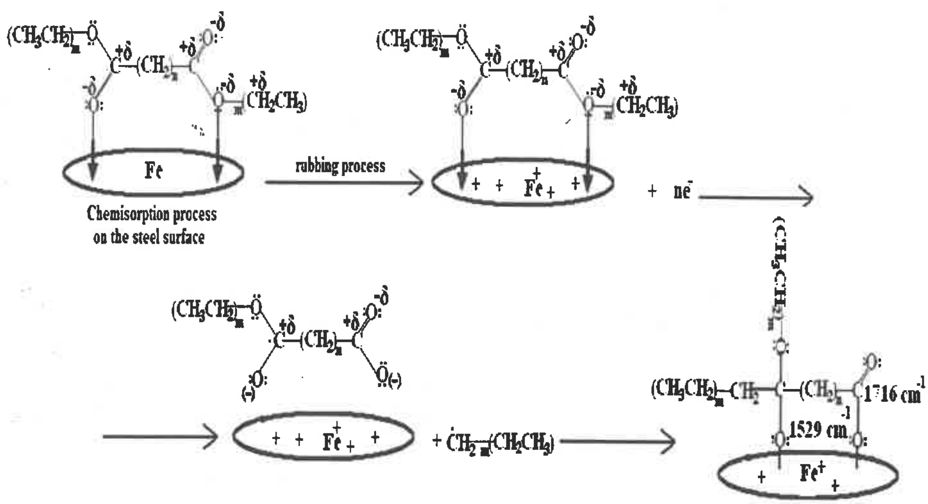


Fig. 3 FTIRM spectrum of the deposit accumulated on steel disk during friction lubricated with pure diethyl succinate.

According to the NIRAM approach, the tribochemical process of steel-on-steel lubricated with diesters may proceed as follows:-



CONCLUSIONS

The effect of aliphatic diester on wear of the steel ball sliding on steel disc can be as follows:

1- The ball wear decreases as the molecular weight of diester increase.
2- The molecular weight of the diester increases as the diacid alkyl or alcohol alkyl chain increases which gave almost the same effective antiwear properties.
3- Using FTIR surface analysis new absorption bands were found in deposits formed on the steel substrate. These absorption bands encompass mostly the region of 1529 cm^{-1}, with usually is combined with the absorption peaks around 1716 cm^{-1}. They have been assigned to organometallic compounds including carbonyl group. This finding clearly confirms tribochemical reactions of low molecular weight of diesters.

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