Applied Surface Science 428 (2018) 659–668

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full length article

Diallyl disulphide as natural organosulphur friction modifier via the in-situ tribo-chemical formation of tungsten disulphide

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ARTICLE INFO

Article history:
Received 17 May 2017
Received in revised form 1 September 2017
Accepted 13 September 2017
Available online 14 September 2017

Keywords:
Diallyl disulphide
Tungsten carbide
Organosulphur compound
Friction modifier
Tungsten disulphide

ABSTRACT

The present work shows a novel method for generating in-situ low friction tribofilms containing tungsten disulphide in lubricated contacts using diallyl disulphide as sulphur precursor. The approach relies on the tribo-chemical interaction between the diallyl disulphide and a surface containing embedded sub-micrometer tungsten carbide particles. The results show that upon sliding contact between diallyl disulphide and the tungsten-containing surface, the coefficient of friction drops to values below 0.05 after an induction period. The reason for the reduction in friction is due to tribo-chemical reactions that leads to the in-situ formation of a complex tribofilm that contains iron and tungsten components. X-ray photoelectron spectroscopy analyses indicate the presence of tungsten disulphide at the contact interface, thus justifying the low coefficient of friction achieved during the sliding experiments. It was proven that the low friction tribofilms can only be formed by the coexistence of tungsten and sulphur species, thus highlighting the synergy between diallyl disulphide and the tungsten-containing surface. The concept of functionalizing surfaces to react with specific additives opens up a wide range of possibilities, which allows tuning on-site surfaces to target additive interactions.

1. Introduction

The reduction of friction in lubricated sliding components is a target pursued in order to reduce energy consumption and, as a consequence, our CO_2 footprint. In order to achieve this goal, modern lubricants rely on functional additives in order to improve the properties of base oils. However, most of the commonly used additives pose environmental concerns more or less, in particular those composed of organic phosphorous, zinc and sulphur [1]. In recent years, nano-particles composed of transition metal dichalcogenides (TMDs) – such as MoS_2 and WS_2 – form emerged as potential substitutes of friction modifiers and anti-wear additives. TMDs have a lamellar structure with a strong bonding between the metal and chalcogenide atoms which contrasts with the weak chalcogenide–chalcogenide interaction between the layers, allowing them to easily slide over each other. This mechanism makes TMDs suitable to be used as solid lubricants. TMDs can be obtained as nanoparticles in several morphologies, such as inorganic fullerenes or nanotubes [2–5]. In both cases, when mixed with additive-free oils such as poly-alpha-olefin (PAO), TMD nanoparticles are able to substantially reduce friction [6,7]. Among the main advantage of TMDs nanoparticles are their inertness, non-toxicity [8] and high thermal stability [9]. However, the interaction between TMD nanoparticles and conventional additives has been seldom investigated. While TMD nanoparticles seem to have a synergistic effect with ZDDP antiwear additive [10,11], their interaction with dispersants is antagonistic [12]. The latter point is crucial since dispersants are required for maintaining the lubrication performances.

TMDs can also be applied directly to tribological components by various techniques. Magnetron sputtering is one of the most commonly used methods that is particularly employed in space applications, due to the excellent coating quality and good bonding with the substrate. Recently, W-S-C coatings doped with a large variety of metals have been proposed for enhancing the mechanical properties of TMDs coatings, while maintaining their low friction properties [13]. The major drawback of TMDs coatings in general is their poor performance in humid air, which limits their use mostly for vacuum and/or space applications.

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http://dx.doi.org/10.1016/j.apsusc.2017.09.100
0169-4332/

TMD tribofilms, in particular WS_2, can also be formed by many different routes involving coatings, bulk materials and fluids containing W and S in different states but not necessarily including crystalline WS_2. A summary of these routes was recently reviewed by Gustavsson and Jacobson [14]. One of these routes relies on the synergy between W-doped DLC coatings lubricated with S-containing additives [15,16]. In this case the reduction in friction achieved under reciprocating sliding is rather modest (0.24 down to 0.15) and a major drawback is the consumption of the coating during the tribochemical reaction. A recent alternative to overcome this problem relies in the in-situ generation of WS_2 using surfaces containing tungsten carbide embedded submicron particles. By these means, WS_2 can be formed at the contact interface through tribo-chemical reactions, thus leading to the same low friction values (~0.05) as those observed in TMD coatings but that are independent of humidity [17]. Furthermore, this method proved to be effective in overcoming the challenge of bringing the nanoparticles into the contact area in the presence of dispersants, since the W-containing particles are already initially embedded on the surface thus making dispersants superfluous. While this approach is promising and can be readily implemented in various engineering applications, the extreme pressure (EP) additives used as sulphur carrier in this study were sulphurised olefins. It has been reported that these type of EP additives may pose environmental concerns, in particular during their manufacturing process that requires the use of sulphur monochloride which leads to the presence of chlorine residues in the final product [18]. For this reason, the current study reports new fundamental insights regarding the in-situ generation of W-S containing tribofilms using lubricant additives that are conformed to the principles of green chemistry [19].

The aim of the present work is the in-situ generation of low friction W-S containing tribofilms using natural organosulphur compounds. The selected natural organosulphur compound, diallyl disulphide, is inexpensive and typically used in the food industry. Further, since food additives are foreseen to be used for human consumption, the toxicity and bioaccumulative properties of such compounds are thoroughly investigated, continuously monitored [20] and strictly regulated [21].

Diallyl disulphide is a non-polar organic compound typically found in garlic that is responsible for its characteristic odour. Diallyl disulphide is soluble in fats, oils and non-polar solvents such as hexane. Diallyl disulphide has been linked with potential health benefits, in particular with a reduction of cardiovascular diseases and some types of cancer [22]. The compound is green to the environment and it can be found on environmentally friendly nematicides [23]. It is also used in the food industry to improve the smell and taste of products. So far, only a single reference could be found in literature, where diallyl-disulphide was used in tribological applications, in particular as one of the components of natural garlic oil proposed as extreme pressure additive [24]. In this work, we exploit the presence of diallyl disulphide for generating in-situ WS_2 under the presence of WC functionalised surfaces. The use of natural organosulphur compounds as lubricant additives in combination with WC functionalized surfaces offers a novel potential application as friction modifiers for this environmentally safe compound.

2. Experimental

2.1. Lubricant mixtures and WC functionalized surfaces

The lubricant mixtures were prepared using commercially available diallyl disulphide (4,5-dithia-1,7-octadiene, Sigma Aldrich, USA) (Fig. 1). The diallyl disulphide was mixed in poly-alpha-olefin 8 base oil (PAO), which was used as the carrier fluid. PAO is a common synthetic base oil that is widely used in industrial components as well as automotive industry. The PAO base oil had a viscosity of 45.5 and 7.9 mm^2/s at 40 and 100 °C, respectively. Its viscosity index (VI) according to ASTM D2270-04 was 146.2 and the density at 15 °C was 0.83 g/cm^3. All the physical properties of the PAO base oil were obtained with a Stabinger viscometer SVM 3000 (Anton Paar GmbH, Austria). The prepared mixtures had a concentration of 1.5 and 10 wt% diallyl disulphide. Since diallyl disulphide is soluble in hydrocarbon oils, the mixture of PAO and diallyl disulphide was stable for al concentrations and no phase separation was observed even after 3 weeks after its initial formulation.

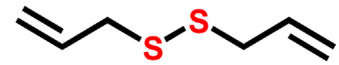

Fig. 1. Molecular structure of diallyl disulphide.

Table 1
Summary of the test parameters.

Normal load	10 N
Stroke	2 mm
Frequency	25 Hz
Test duration	14400 s
Counterbody	100Cr6 Ball
Ball diameter	10 mm

Stainless steel AISI 304 surfaces were functionalized by embedding tungsten carbide (WC) particles with a diameter of 0.8 μm using a machine hammer peening technique [25]. The WC particles were mixed with non-additivated oil until forming a homogeneous suspension, which was deposited on the surface of the steel samples. Afterwards, the sample was peened at a 90° angle with a hammer equipped with a semi-spherical WC ball (8 mm diameter) along a predefined path using an impact frequency of 200 Hz (Fig. 2). The impact energy of the hammer on the oil suspension resulted in the WC particles being mechanically embedded into the surface of the steel. The sample was peened line by line until the complete steel surface was hit by the hammer. The process was repeated twice in order to achieve a final surface coverage by the WC particles of 20%. A thorough description of the embedding process along with a detailed characterisation of the resulting functionalized surfaces can be found elsewhere [26].

2.2. Tribological evaluation

The tribological performance of the lubricant mixtures was evaluated under reciprocating sliding conditions using an SRV® tribometer (Optimol, Germany). The tests were performed at an oscillating frequency of 25 Hz with a stroke of 2 mm. As counterbody, a 10 mm diameter 100Cr6 bearing steel ball was used. The normal load was set to 10 N. The tribological tests were performed at room temperature, following the testing parameters of our preliminary work (Table 1) [17]. Prior to the tests, tungsten carbide containing surfaces and the bearing steel balls were cleaned for 10 min in ultrasonic bath using toluene and petroleum ether. Afterwards the WC functionalized surfaces were tested for four hours under fully immersed contact conditions using 0.2 ml of lubricant mixture. Throughout the test, the coefficient of friction was recorded.

2.3. Morphological and chemical analyses of the tribofilms

Scanning electron microscopy (SEM) with energy dispersive x-ray analyses (EDX) was used for evaluating the morphology and elemental composition of the generated tribofilms. A JEOL JSM 6500 F (Jeol, Japan) was operated using an acceleration voltage of 20 kV. The SEM was used in secondary electron and in backscattered