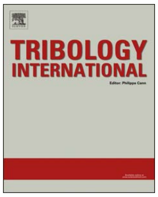
Tribology International 107 (2017) 144–151

Contents lists available at ScienceDirect

Tribology International

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



A new concept of the mechanism of tribocatalytic reactions induced by mechanical forces

Czesław Kajdas[a], Andrzej Kulczycki[b], Dariusz Ozimina[c]

[a] Faculty of Civil Engineering, Mechanics and Petrochemistry, Institute of Chemistry, Warsaw University of Technology, Branch in Płock, ul. Łukasiewicza 1, 09-400 Płock, Poland
[b] Air Force Institute of Technology, ul. Księcia Bolesława 6, 01-494 Warszawa, Poland
[c] Faculty of Mechatronics and Mechanical Engineering, Kielce University of Technology, al.1000-lecia PP. 7, 25-314 Kielce, Poland

ARTICLE INFO

Keywords:
Triboreactions
Energy distribution
Boundary lubrication

ABSTRACT

The aim of this paper is to present a new approach to the mechanism of tribocatalytic reactions induced by mechanical forces. The new concept is based on the authors' previous research, which reveals that there exists a relationship between the modified coefficient of reagent reactivity α_i, the ratio of mechanical forces acting on a tribological system and a change in the internal energy of a lubricant (including a thin boundary layer).

$\alpha_i=(L-L_0)/\ A\ \exp[-E_a/(RT+\varepsilon)]\ [(e_0)\ \cos\ (k_2L+k_3)]\ t$

and $1/\ A\ \exp[-E_a/(RT+\varepsilon)]\ [(e_0)\ \cos\ (k_2L+k_3)]\ t = C$

The paper has been divided into two parts. Part One provides a theoretical analysis of the distribution of energy between a solid surface and the molecules of a lubricant during a tribological process. This part concludes with the formulation of three hypotheses: first, that the tribocatalyst transforms mechanical energy into a flux of electrons and/or photons, which provide additional amounts of energy to the molecules of the reagents, secondly, that the function C describes a wave of energy understood as a wave-like change in the internal energy of a tribological system caused by an increase in the applied load and, thirdly, that a chemical reaction can be initiated when i) the molecules of the reagent are supplied with energy equal to the activation energy E_a and ii) the energy is supplied by a sufficiently high flux.

Part Two discusses the empirical data that initially confirm the above hypotheses. The evidence combines i) the experimental results concerning the emission of electrons during friction with ii) the test results obtained for a number of lubricating oils using the Timken apparatus and method.

1. Introduction

In tribological systems, it is essential that a sufficient amount of energy be supplied to contact surfaces to overcome the resistance attributable to the phenomenon of friction. Friction causes this energy to split, transform, accumulate and dissipate. Dissipation, which is an irreversible process, is related to energy flow.

Friction results in losses of mechanical energy, transformations in the materials in contact, heat release and triboelectric charging. As the losses are measurable, researchers are focusing on how to rationally use the energy. They are also trying to understand and precisely define all the phenomena and processes accompanying friction in order to increase the efficiency of triboreactions in various tribological systems.

Fig. 1 shows the basic types of energy occurring during friction and their possible transformations. In a classic tribological system, energy is generally present in the form of heat, which may be transformed to another form [1,2].

The energy balance Eq. (1) can thus be written as:

$$\Sigma E_X = \Sigma E_Y + \Sigma E_S + \Sigma E_Z + \Sigma E_T \qquad (1)$$

where: E_X – input energy; E_Y – output useful energy; E_S – non-thermal energy lost; E_Z – energy accumulated; E_T – energy transformed into heat.

This equation describes the energy state in a tribological system. The use of first order equations enables us to determine, in an integrated way, the instantaneous state of a tribosystem by specifying the boundary conditions for a particular case and application [1].

The rapid energy transformations associated with friction lead to the wear of the surface layers in the contact zone followed by the occurrence of tribochemical processes, which contribute to the formation of a tribofilm preventing further surface damage and providing effective lubrication under specific rubbing conditions. The common

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E-mail addresses: ckajdas@pw.plock.pl (C. Kajdas), andrzej.kulczycki@itwl.pl (A. Kulczycki), ozimina@tu.kielce.pl (D. Ozimina).

http://dx.doi.org/10.1016/j.triboint.2016.08.022
Received 20 June 2016; Received in revised form 17 August 2016; Accepted 19 August 2016

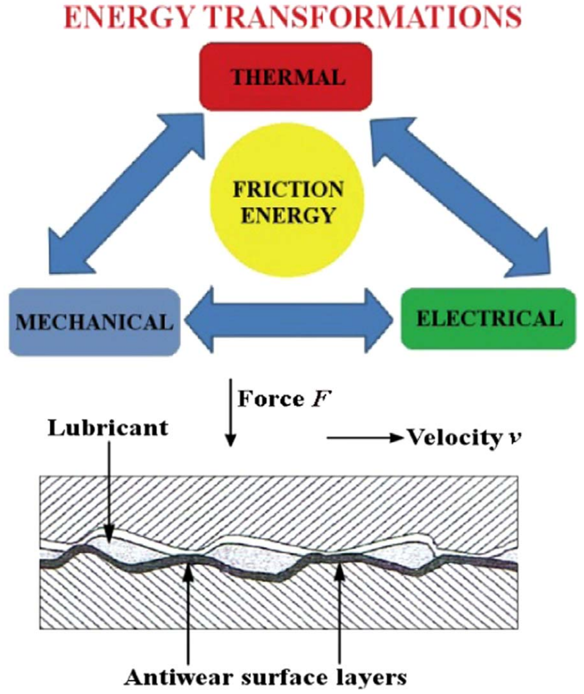

Fig. 1. Main forms of energy occurring during friction between the elements of a tribosystem [1].

feature of all tribological systems is that the equilibrium state is dependent on the thermodynamic factors. An example of a manufacturing process during which extreme tribological states occur in the material and its surface layer is metal cutting, classified as a tribotechnology [3,4].

Obviously, in the majority of cases, the largest part of the mechanical energy is dissipated as heat and mechanical vibration, which is then transformed to sound waves. The thermal and non-thermal (mechanical and/or electrical) energy generated during friction activates tribochemical processes in a tribological system. The energy is also responsible for the changes in the properties and energy state of the boundary layer, the modifications of the mechanical properties of the surface layers in the contact zone resulting from the changes in the material structure, and, finally, the formation of an antiwear tribofilm.

The complexity of the friction phenomenon and related processes makes it difficult for researchers to create a universal mathematical model describing the interactions between the elements and components of tribological systems that occur during friction [1].

The lubricity of lubricating oils and fuels is one of the most important factors affecting the performance and durability of machines. The term is related to boundary and mixed lubrication as well as lubricating additives, i.e., compounds that undergo adsorption and chemisorption on the surface of lubricated machine elements. There are many chemical compounds which, when added to a lubricating oil (e.g., ZDDPs and sulfur compounds) or a fuel (e.g., oxygen compounds) at a concentration of 100 ppm up to several percent, react to form a durable layer protecting the lubricated elements against wear and seizure. The mechanism of the protective layer formation is very important and there are many articles and books available on this topic. The research on lubricity spans the disciplines of mechanics, physics and chemistry. Various models of the boundary layer have been developed, but none is suitable to predict its durability for a particular machine or specific operating conditions. Moreover, no model takes into account interactions between the additives and the other compounds of the lubricating oil or fuel or the surface properties of the lubricated elements other than hardness and roughness.

This suggests that lubricity is a qualitative parameter determined as the wear or seizure of the tribometer elements resulting from the applied load. It is possible to compare the lubricity of different lubricants (lubricating oils or fuels) when the same tribometer and the same test procedure are used. It is impossible, however, to predict which lubricating oil or fuel will offer the best protection of elements against wear or seizure when different tribometers or machines are employed. Results obtained with one type of tribometer can be converted into results obtained by means of another when, in both tribotests, lubricity is determined using the same or a universal parameter. In the tribology of the boundary layer, there is no such parameter as, for instance, the coefficient of viscosity in rheology, to be used to quantitatively describe hydrodynamic lubrication [5]. The generalized Reynolds equation

$$\delta/\delta x\,(h^3\delta p/\delta x) + \delta/\delta z\,(h^3\delta p/\delta z) = 6\eta(\mathrm{U}_1 - U_2)\delta h/\delta x \tag{2}$$

links the macroscopic, mechanical parameter, i.e., the thickness of the hydrodynamic film, h, and the difference in the speed of rotation between the pin and the bushing (U_1 and U_2, respectively), both representing action, to the coefficient of viscosity η, a parameter dependent on the interactions between the lubricant molecules, defined and described at the molecular level.

2. Review of previous results

In the 80s, Kulczycki [6] introduced into the tribology of boundary lubrication a new measure of lubricating additive effectiveness/reactivity – the dimensionless coefficient α_i. This relative coefficient of reactivity was described by the relationship of two functions of one variable, for instance, the seizure load:

$$\alpha_i = \{[\mathrm{f(a)} - f\,(\mathrm{b})]/[\phi\,(\mathrm{a}) - \phi\,(\mathrm{b})]\}\,\mathrm{d}\phi\,(\mathrm{a})/d\,(f\,(\mathrm{a}) \tag{3}$$

where: f(a) – function describing action, i.e., the force necessary to cause destruction of the protective layer in the analyzed system (a lubricant containing a specific additive or component), f(b) – function describing the force necessary to cause destruction of the protective layer in the reference system, ϕ(a) – function describing the reaction in the analyzed system, and ϕ(b) – function describing the reaction in the reference system. The coefficient α_i is a relative measure of the lubricant/lubricating additive effectiveness in the boundary layer formation. The authors of this paper assume that, due to relativity, Eq. (3) describes the lubricant, including the boundary protective layer, as part of the tribological system (see Fig. 2). The analyzed tribological system comprising a lubricant with an additive is related to the reference system, which can contain a reference lubricant, for instance, a lubricant without an additive.

It has been found that assuming the function f(y), where y =(a, b), we can determine the function ϕ(y). This will help better understand the mechanism of the boundary layer formation by lubricating additives, which can be applied to formulate lubricating oils and fuels. Relationship (3) makes it possible to generalize the results of numerous detailed studies of tribochemistry and interactions between gaseous/liquid reagents and a solid catalyst/tribocatalyst (see Section 3: "Initial verification of the proposed mechanism of catalyzed triboreactions").

Since the analysis of the boundary layer is generally based on the results of a four-ball test, the seizure and weld loads are assumed to be represented by the variable y. The methods described in [6] were applied

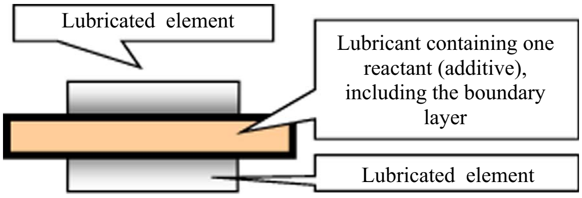

Fig. 2. Tribological system described by the α_i model.