Chapter

Green Tribology

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Abstract

This chapter provides an overview of Green tribology, which is a new direction in the development of tribology, a new interesting area for scientific researches and a new way to turn tribology into a friend of ecological environment and saving energy. Green tribology is considered as well as close area with other "green" disciplines like green engineering and green chemistry. In the chapter, the various aspects of green tribology such as the concept, perspectives, role and goal, main principles, primary areas, challenges and directions of the future development have been discussed. It was clarified that green tribology can be defined as an interdisciplinary field attributed to the broad induction of various concepts such as energy, materials science, green lubrication, and environmental science. The most important role and goal of green tribology is improvement of efficiency by minimizing wear and friction in tribological processes to save energy, resources and protect environment, and consequently, improve the quality of human life. The twelve principles and three areas of green tribology were analyzed. Observation of these principles can greatly reduce the environmental impact of tribological processes, assist economic development and, as a result, improve the quality of life. The integration of these areas remains the major challenge of green tribology and defines the future directions of research in this field. This work also presents a rather detailed analysis of the most important effect in green tribology—the "zero-wear" effect (selective transfer effect). It was established that the "zero-wear" effect is due to self-organization in frictional interaction in tribological systems, which is the consequence of the complex tribo-chemical reactions and physico-chemical processes occurred in the area of frictional contact, that lead to the manifestation of unique tribological characteristics: super-antifrictional (friction coefficient ~ 10^{-3}) and without wear (intensity wear ~10^{-15}). This condition of tribo-system was provided by a protective nanocrystalline servovite film made of soft metal with unusual combination of mechanical properties.

Keywords: green tribology, friction, lubricants, wearlessness, zero-wear, selective transfer, biomimetics, self-lubrication, surface texturing, renewable energy

1. Introduction

Today, environmental and energy problems have become extremely serious and survival on a global scale. Scientists in all fields pay great attention to solving these problems. By this logic, the boom of recent decades, associated with the formation and development of nanotechnologies, including in relation to tribology and tribotechnics [1, 2].

It is noticeable that tribology has continuously developed into new phases. After opening in 1956, the effect of selective transfer (ST) ("zero-wear" effect) during friction, in tribology for the first time, was a basis to build the whole new paradigm of "friction without wear with minimal energy consumption", which was denied by all previous practical experience in operating movable coupling and by theoretical constructions of science of the friction and wear solids. At the same time, by the beginning of this century, the concept of "green tribology" was formed, which actually lists all the achievements in the study of the mechanisms of wearlessness (zero-wear) and super-anti-friction, as well as in the development of lubricants for their implementation in practice [3, 4]. In the 21st century and beyond, green tribology is expected to play an increasingly important role and become the key and strategies for solving a series of global problems in energy, environment and resources.

In recent years, there has been a rapid growth in research activities in green tribology field. A fairly large number of articles, world conference reports and academic books in related to this area have been published [2, 5–15]. However, there are still few publications that expounded the concepts, technological connotations, principles and disciplinary features of green tribology in precise, comprehensive definition and in an all-round way. The first scientific work completely devoted to green tribology, which emphasized the scientific rather than the economic and social aspects was published by M. Nosonovsky and B. Bhushan in 2010 [5].

Being a new field of tribology still in its infancy, an accurate understanding of the fundamentals of green tribology is important from both a scientific and practical point of view. In this regard, the aim of this work is to clarify the fundamental scientific and technological foundations of green tribology based on the analysis and generalization of the research achievements of green tribology.

2. Green tribology: concept, goal and role

It has been noted that the concepts in the main development direction of tribology are historically changed as follows (**Figure 1**).

Nowadays, the term "green tribology" has become part of the engineering dictionary. Green tribology is an emerging and actual area in tribological science with more focus on energy saving and environmental protection. Although green tribology is a fairly new concept; however, it already plays an important role in ensuring that all industrial systems can be able to function in an environmentally friendly manner. Green tribology is especially tuned to sustaining an ecological balance and biological effects on contact between surface systems from different materials. Green tribology ensures that any process of friction and wear is as environmentally friendly as possible. Thus, green tribology can be defined as an interdisciplinary field attributed to the broad induction of various concepts such as energy, materials science, green lubrication, and environmental science [8–11].

We have known the concept of green engineering for a long time. The United States Environmental Protection Agency (USEPA) defines green engineering as

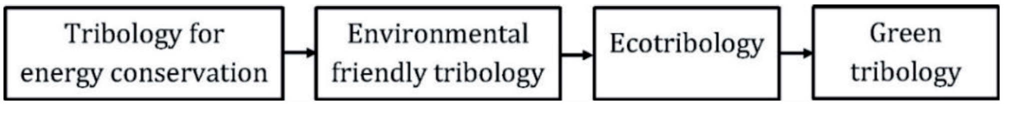

Figure 1.
Tribology concepts in the new main direction of development [1, 2].

"the design, commercialization and application of processes and products that technically and economically reduce sources of pollution and risks that adversely affect human health and the environment". Speaking of green tribology, one cannot ignore the terms "Green Technology", "Green Engineering", "Green Metalworking", etc., but the first association and historically, the first green science, as applied to science naturally, was "Green Chemistry". Green engineering and green chemistry are two closely related fields of green tribology that are actively engaged by researchers today [12, 13].

Specifically, green tribology has been identified as an area of engineering that could go beyond its original remit of improving efficiency by minimizing wear and friction in tribological processes to save energy and resources, minimize noise pollution, develop new bio-lubricants. In general, green tribology gives a positive contribution in reducing environmental harm. Inevitably, the term "green tribology" is spoken of in the context of quality of life. According to professor's Zhang opinion [2]: "Thus, the concepts and objectives of green tribology might be summarized into 3L + 1H, namely, low energy consumption, low discharge (CO_2), low environmental cost, and high quality of life. The mission of green tribology is researching and developing tribological technologies to reach the main objectives, thus making the sustained artificial ecosystems of the tribological parts and tribosystems in the course of a lifecycle".

Emilia Assenova and her colleagues in their work "Green tribology and quality of life" [14] reported: "Nowadays, losses resulting from ignorance of tribology amount to about 6% of the gross national product (GNP) in the United States alone. This figure is around USD 900 milliard annually. As far as China is concerned, they could save above USD 40 milliard per year by the application of green tribology or more than 1.5% of the GNP". It is clear that the basic goals of green tribology are "friction control, wear reduction and improved lubrication". Nevertheless, from a socio-economic point of view, it is possible to extend and confirm that the goal and essence of research works in the field of green tribology is to save material resources, improve energy efficiency, decrease emissions, shock absorption, investigate and apply novel natural bio- and eco-lubricants as well as to reduce the harmful effects of technical systems on the environment, and consequently, improve the quality and welfare of society. All advances in green tribology will lead to a high economic efficiency due to reduced waste and increased equipment service life, improved technological and environmental balance, decreased carbon footprint of mechanical systems, as a result, mitigate climate changes, and improve overall sustainability and safety in human life [15].

Green tribology will play an irreplaceable role in saving energy, material resources and environment. Trusted researches reveal that about 23% of energy consumption in the world today is the result of inefficient performance of tribological systems (**Figure 2**) [16]. In this case, approximately 18–20% of the energy is consumed to solve friction problems, and the remaining 3–5% is used to rebuild, repair and replace parts worn out due to wear and other failures associated with wear. The researchers estimated that by applying advances in green tribology in terms of new surfaces, materials and lubrication technologies, the total global energy loss in tribological systems could be decreased by 18% in the next 8 years and up to 40% in the next 15 years. An additional advantage of environmentally friendly green tribology is a significant reduction in carbon dioxide emissions and economic costs.

In works [17–23] the researchers applied green tribology concept using new class of eco-friendly lubricants and materials for manufacturing anti-friction contact surfaces, as a result of which their coefficient of friction is significantly reduced while the wear resistance and longevity are greatly increased.

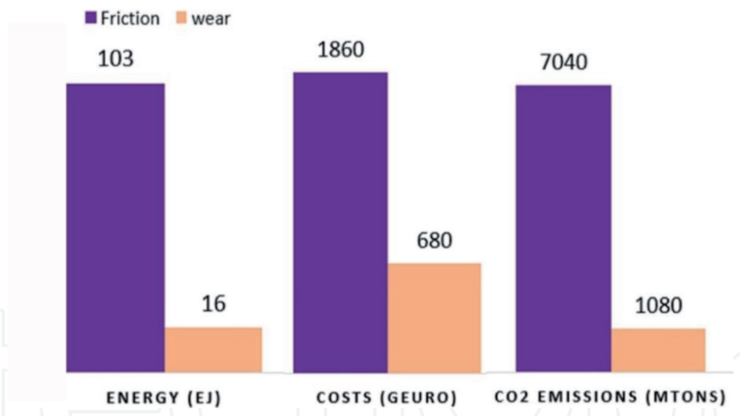

Figure 2.
Energy consumption, costs and CO_2 emissions due to inefficient performance of tribological systems globally [16].

A survey of gross energy consumption in the United States in four main areas: transportation, turbomachinery, power generation and industrial applications showed that savings of about 11% are achieved thanks to recent developments in lubrication and green tribology [24]. Chinese estimated that they could save more than $ 40 billion per year by applying advances in green tribology [25].

If we look at the share of wind energy in the total installed electricity capacity in Europe over the last decade, according to the European Wind Energy Association, it has increased more than quadrupled from 2.2% in 2000 to 10.5% in 2011 thanks to new developments in tribology, in particular as a result of the application of green tribology [26].

Many tribological problems can be put under the umbrella of "green tribology" and are mutually beneficial to each other. These problems are primary focus point of researchers and engineers, which include tribological technology that mimics living nature (biomimetic surfaces) and thus is expected to be environment-friendly, the friction and wear control that is important for energy conservation and conversion, environmental aspects of lubrication and surface modification techniques. These problems and aspects will be clarified in more detail in the next section.

3. Green tribology: principles, focus areas, and challenges

3.1 Principles of green tribology

As noted above, the interdisciplinary nature of green tribology often integrates aspects of chemical engineering and materials science in order to completely understand both chemistry and mechanics of surface. Since tribology is an interdisciplinary field, the principles of green engineering and green chemistry should also apply to green tribology. However, tribology includes not only chemistry of surfaces, but also other aspects related to the mechanics and physics of surfaces, there is a need to modify these principles.

Formulated by Paul Anastas in 1991, the 12 principles of green chemistry into a constant amount (12) upgraded to the 12 principles of green engineering [27, 28], and later, in the 12 principles of green tribology [1] mapped in **Table 1**.

These principles of green tribology can be assorted into 5 following groups: Friction, Wear, Lubrication, Material and surface production and treatment, and Tribology in the renewable energy sources.

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Green chemistry	Green engineering	Green tribology
• Prevention. • Atom Economy. • Less Hazardous Chemical Syntheses. • Designing Safer Chemicals. • Safer Solvents and Auxiliaries. • Design for Energy Efficiency. • Reduce Derivatives. • Catalysis. • Design for Degradation. • Real-time analysis for Pollution. • Prevention. • Inherently Safer. • Chemistry for Accident Prevention.	• Inherent rather than circumstantial. • Prevention instead of treatment. • Design for separation. • Maximize mass, energy, space, and time efficiency. • Output-pulled versus input-pushed. • Conserve complexity. • Durability rather than immortality. • Meet need, minimize excess. • Minimize material diversity. • Integrate local material and energy flows. • Design for commercial "afterlife". • Renewable rather than depleting.	• Minimization of heat and energy dissipation. • Minimization of wear. • Reduction or complete elimination of lubrication and self-lubrication. • Natural lubrication. • Biodegradable lubrication. • Sustainable chemistry and green engineering principles. • Biomimetic approach. • Surface texturing. • Environmental implications of coatings. • Design for degradation. • Real-time monitoring. • Sustainable energy applications.

Table 1.
12 principles of green chemistry, green machine building and green tribology.

Friction *(minimization of heat and energy dissipation)*. Friction is the main source of energy dissipation, most of which is converted to heat. Controlling and minimizing friction, which results in both energy savings and the prevention of damage to the environment owing to heat pollution, is a top priority for green tribology. In addition, the friction in mechanical systems that operate on friction, such as clutches and brakes, also has to be well optimized.

Wear *(minimization of wear)*. This is the second most important task of green tribology. In most technological processes, wear is undesirable, it decreases the lifetime of elements/machine and creates the problems of their recycling/replacements which in turn leads to environmental damage by way of the emission. Wear can also lead to a large waste of material resources. In addition, due to wear, debris in the form of particles is generated, which pollutes the environment and in certain situations can be dangerous to humans.

Lubrication. *Reduction or complete elimination of lubrication and self-lubrication*. Lubrication is at the forefront of tribology as it reduces friction and wear. However, lubrication is also hazardous to the environment. It is desirable to reduce the use of lubricants or achieve a self-lubrication regime when no external lubrication is required. Tribological systems in living nature often operate in the self-lubricating mode. For example, the joints form a closed, self-sufficient system. Green tribology prompted researchers to think about self-lubricating materials, which also eliminated the external supply of lubricants.

Natural lubrication. In green tribology Natural lubricants such as vegetable oils should be used in cases when possible, since they are eco-friendly.

Biodegradable lubrication. Biodegradable lubricants should also be used when possible to avoid environmental pollution. In particular, water lubrication is an area that has attracted the attention of tribologists in recent years. Lubrication with natural oils is another good option.

Material and surface production and treatment. *Sustainable chemistry and green engineering principles*. These principles should be observed in the production of new materials, elements, parts, machines for tribological applications, coatings and lubricants.

Biomimetic approach. Wherever possible, biomimetic surfaces and materials, as well as other biomimetic and biological approaches, should be applied as they tend to be more environmentally friendly. Common engineered surfaces have occasional roughness, which makes friction and wear extremely difficult to overcome. On the other hand, many biological functional surfaces have complex structures with hierarchical roughness that determines their good properties for tribological systems.

Surface texturing. This technology should be used to provides a way to control many surface properties relevant to making tribo-systems more ecologically friendly.

Environmental implications of coatings. Environmental implications of coatings and other methods of surface modification (texturing, depositions, etc.) should be studied and taken into consideration.

Design for degradation. The ultimate degradation and utilization of contact surfaces, coatings, and tribological components should be considered during design.

Real-time monitoring. Tribological systems should be analyzed and monitored during operation to prevent the formation of hazardous substances.

Renewable energy sources (*Sustainable energy applications).* Sustainable energy applications should be a priority direction for tribological design, as well as engineering design in general.

Correct observation of discussed above principles of green tribology can greatly reduce the environmental impact of tribological process's products, assist economic development and, consequently, improve respectively the quality of life.

3.2 Focus areas of green tribology

Green tribology includes 3 main areas [1, 2, 5, 14], these are (1) Biomimetics (imitating living nature in order to solve complex human problems) and self-lubricating materials/surfaces; (2) Biodegradable and environmentally friendly lubrication and materials; and (3) Renewable and/or sustainable sources of energy. These 3 focus areas of green tribology aim to ensure a limited impact of tribological processes on the environment and human health. Below is a brief description and discussion about the features, contents, aspects of these areas and their relevance to green tribology.

Biomimetic and self-lubricating materials/surfaces. This is an important area of green tribology, the main task of which is the development and application of tribological technologies that mimic living nature (biomimetic surfaces). Many biological materials have amazing properties (superhydrophobicity, self-cleaning, self-healing, high adhesion, reversible adhesion, high mechanical strength, antireflection, etc.) that can hardly be achieved by conventional engineering methods. These properties of biological and biomimetic materials are reached due to their composite structure and hierarchical multiscale organization. It is noted that hierarchical organization and the ability of biological systems to grow and adapt also ensure a natural mechanism for the repair or healing of insignificant damage in the material. Biomimetic materials are also usually environmentally friendly in a natural way, since they are a natural part of the ecosystem. For this reason, the biomimetic approach in green tribology is especially promising.

In the field of biomimetic surfaces, a number of typical ideas have been proposed: (1) *The lotus effect based non-adhesive surfaces; (2) The Gecko effect based materials with the ability of specially structured hierarchical surfaces to* *exhibit controlled adhesion; (3) Fish-scale effect based micro-structured surfaces for underwater applications, including easy flow due to boundary slip, the suppression of turbulence and anti-biofouling; (4) Oleophobic surfaces capable of repelling organic liquids; (5) Microtextured surfaces for de-icing and anti-icing; (6) Various biomimetic microtextured surfaces to control friction, wear and lubrication; (7) Self-lubricating surfaces, using various principles, including the ability for friction-induced self-organization; (8) Self-repairing surfaces and materials, which are able to heal minor damage (cracks, voids); (9) The "sand fish" lizard effect, able to dive and "swim" in loose sand due to special electromechanical properties of its scale; (10) Nanocomposite materials tailored in such way that they can produce required surface properties, such as self-cleaning, self-lubrication, and self-healing.*

Figure 3 shows typical biological and biomimetic surfaces with hair or pillar like surface structures for various functions (**Figure 3**) [29]. Recently, the mechanisms of sand erosion resistance of the desert scorpion were studied to improve the erosion resistance of components in tribo-systems [30]. It was found that the biological surfaces used for sand erosion resistance of the desert scorpion were built by the special micro-textures such as bumps and grooves.

In works [31–33], the authors presented overview and studies of various biomimetic microtextured surfaces to control friction, wear and lubrication. Generally, biomimetic techniques have provided the different surface structures with strong adhesion, high hydrophobic properties, high coefficient of friction, self-lubrication, etc., which can be prospectively applied in green tribology field.

Biodegradable and environmentally friendly lubrication and materials. Advanced biomimetics is biomimicry used to identify best practices from nature on key tribological issues, such as finding improved lubrication solutions [1, 14, 34]. Natural lubrication is very effective at providing low coefficients of friction even at low speeds, and relies entirely on water as the base component, the effectiveness of which is ensured by the presence of many dissolved biomolecules.

Imitating such constructs of molecules, understanding their tribological performance is helpful. An example is the process of imitating natural lubricants, e.g. glycoproteins in synovial fluid [32]. By imitating this mechanism in the laboratory, molecules were synthesized that spontaneously produce polymer brushes on the surface. Brushes are formed on surfaces in an aqueous medium when end-grafted, water-soluble polymers are located at distance about one radius of gyration (Rg) from each other (**Figure 4**) [34] and stretch to maximize their interaction with water while reducing their interaction with each other.

The use of lubricants in machine components poses a serious threat to the environment, since they released into the environment not only contain harmful toxic waste but also contain the wear debris from machine parts. Development of environmentally acceptable lubricant products is one of priority direction in green tribology. Vegetable oils and animal fats have been used as lubricants for a very long time throughout human history. However, following the industrial revolution and the advent of lubricants made from mineral oils, bio-based lubricants have again come to be seen as an environmentally alternative for lubricant production and have only become effective in recent decades.

Researchers confirmed that properly formulated bio-lubricants are comparable with mineral based lubricants, so they could be used as an adequate substitution in appropriate cases. Vegetable-oil-based or animal-fat-based lubricants are potentially biodegradable that can be used for engines, hydraulic and metal-cutting applications. Vegetable oils i.e. corn, soybean and coconut oil, can have excellent lubricity, far superior than that of mineral oil [12, 14]. In general, the advantages of using bio-lubricants are non-toxic, biodegradable, renewable resources, good lubricity and high viscosity indices (**Table 2**) [35], while disadvantages are:

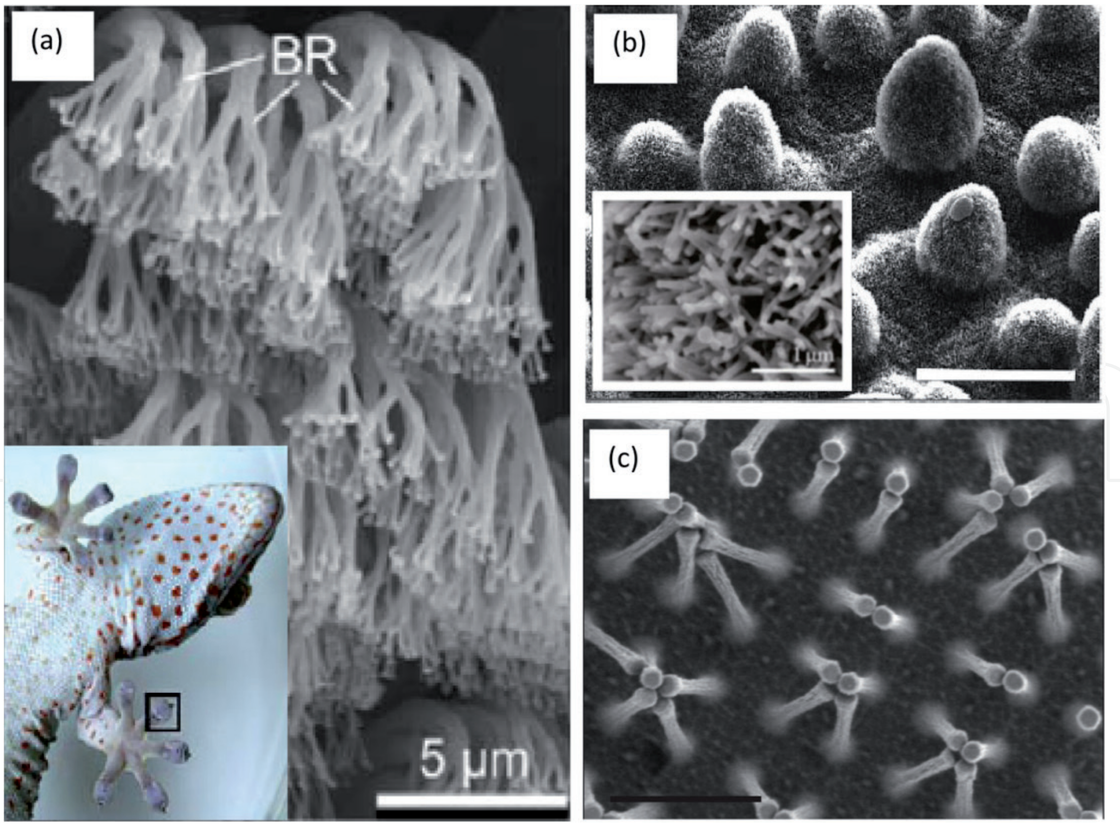

Figure 3.
Typical biological and biomimetic surfaces with hair or pillar like surface structures for various functions. (a) The nano to micro hierarchical hair-like surface structure of geckos' feet for strong adhesion; (b) The nano to micro hierarchical structure of plant leaves for superhydrophobic dewetting properties. (c) The microfabricated polyimide biomimetic hairs bunching together under the van der Waals interaction [29].

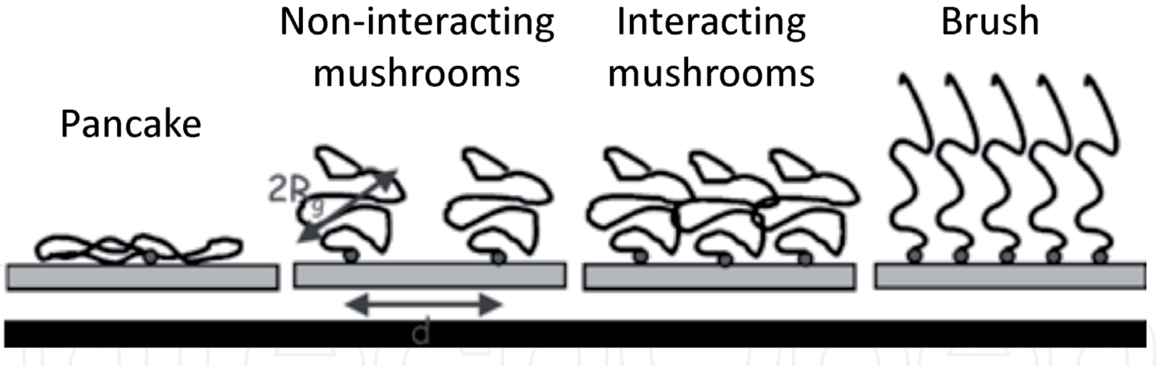

Figure 4.
The formation of polymer brushes on surfaces [34].

oxidative instability, poor low temperature properties, and hydrolytic instability. Applying chemical modification or additives can address these problems of bio-lubricants.

In the area of eco-friendly and biodegradable lubrication and materials we should also notice other following interesting ideas:

Hyrdo-lubrication. These are homogeneous lubricants containing water as a functional component. Tribological study and case analyses of the elastomeric bearings lubricated with seawater for marine propeller shaft systems were conducted [36].

Ionic liquids for green molecular lubrication. Ionic liquids (ILs) have been explored as lubricants for various device applications due to their excellent electrical conductivity as well as good thermal conductivity, where the latter allows frictional heating dissipation [37].

Oil type	Engine oil	Coconut oil	Palm oil
CO_2 (%)	4.5	2.9	3.4
CO (%)	0.92	0.67	0.73

Table 2.
The percentage content of CO and CO_2 in exhaust gas lubricated with regular mineral and vegetable oils [35].

Powder lubrication. Generally, these tend to be much more eco-friendly than the traditional liquid lubricants. Recent researches show that when using some nanoscale additives, such as boric acid and MoS_2 nanopowders to natural oils, their lubricity characteristics are significantly improved [38].

New eco-friendly coating materials for tribological applications. Recently, special attention has been paid to the development of "green" coatings in tribo-systems, which have improved tribological properties (low friction coefficient, high wear resistance), and therefore, not releasing a lot of worn-out waste into the environment, they are environmentally friendly [1, 2, 6].

Tribology in the Renewable Energy Sources (RES). Controlling and minimizing of friction and wear in tribology is important for energy and resources conservation. Sustainable energy applications have become priority of the tribological design, as well as an important area of green tribology. In contrast to the biomimetic approach and environmentally friendly lubrication, RES is not about manufacturing or operation, but about the application of the tribological system in production of renewable eco-friendly energies such as wind energy, marine energy, solar energy, geothermal energy, and so on.

In work [39] Wood et al. carried out the tribological studies on renewable sources of energy, namely three green energy systems: wind, tidal and wave machines. The authors also highlighted the role of design and durability for such large scale engineering systems from sustainability point of view. These systems are sensitive to operation and maintenance costs and thus depend on functioning tribological parts and lubrication. It was noted that weight reduction to reduce tribological and gravity loads would be beneficial for machines designs. Attention should also be paid to the knowing of dynamic loads to predict fatigue life and tribological loads on wind, tidal and wave machines. Structures and properties of tribological components must be considered for the inherent lack of stiffness of the turbines and wave devices.

Wind turbines have fairly many specific problems related to their tribology, which involve water contamination, electric arcing on generator bearings, wear of the main shaft and gearbox bearings and gears, the erosion of blades due to solid particles, cavitation, rain, hail stones, etc. The most commonly observed and discussed tribological problems in wind turbines are in the transmission system, in the gearbox. They are mainly the result of insufficient lubrication and/or lack of regular maintenance under extreme operating conditions. The solution to this problem is the use of lubricants and/or materials with improved tribological characteristics [40]. REWITEC nano-coatings is a metal treatment that can be applied to gearboxes and bearings during regular operation for restoration of its efficiency and economy. When examining certain micro-pitting areas on the metal surfaces of a wind turbine gear before applying REWITEC and after 6 months of treatment, it was found that the surface damage was filled and the asperities were smoothed out, and thus the surfaces became smoother with higher surface contact area (**Figure 5**) [2].

Tidal power turbines are another important way of producing renewable energy. Besides tidal, the ocean water flow and wave energy and river flow energy (without dams) can be used with the application of special turbines, which provides the same

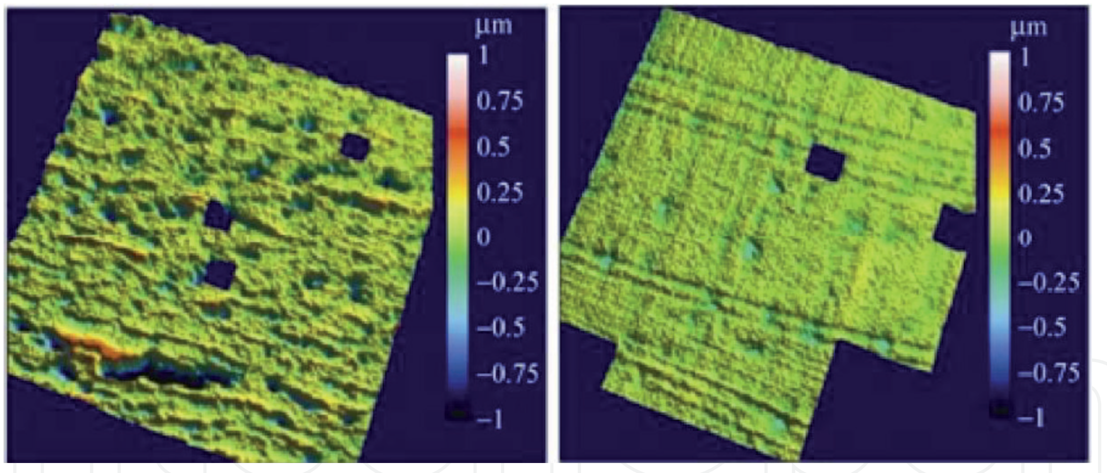

Figure 5.
3D-images of the metal surface before and after treatment with REWITEC 6 months [2].

direction of rotation independent of the direction of the current flow. Production processes of tidal, water flow and wave energy involve certain specific tribological problems such as lubrication of machine components (by seawater, oils, and greases), their erosion, corrosion, and biofouling, as well as the interaction between these modes of damage [1, 39].

Geothermal energy plants are widely used now, however, their application is limited to the geographical areas at the edges of tectonic plates. There are several specific tribological issues related to the geothermal energy sources which are discussed in the literature [1, 5, 15, 39].

3.3 Challenges of green tribology

Green tribology as a new area of tribology has a number of challenges. One obvious problem is integration, synergy of its above mentioned focus areas so that they can benefit from each other. Obviously, a lot of researches is needed to integrate the fields of green tribology. Some ideas can be borrowed from the related fields of green chemistry and green engineering, for example, the development of quantitative parameters for assessing the impact of tribological technologies on the environment. It is also important to develop quantitative measures and metrics that would allow us to compare which tribological material, technology, or application is "greener," i.e., produces lower carbon footprint, less waste from worn-out materials, and less chemical and heat pollution to the environment.

Green tribology should be integrated into world science and contribute to solving global problems such as resource depletion, environmental pollution and climate change. The application of principles of green tribology by itself, of course, will not solve world problems, and only major scientific achievements can become the key to their solution.

In the face of a large number of tribological problems requiring an early solution, which related to the environmental pollution, crisis of energy and resources on global scale, green tribology should be extended in the following directions [2].

- Large-scale deployment of existing knowledge, methods, and technologies of green tribology;
- Research and development of novel green tribological technologies;
- Research and development of tribo-techniques to support diversification and hybridization of renewable and clean energy;

- Making the traditional tribo-materials and lubricating materials "green" in the course of a lifecycle, namely, realizing cleaner production or eco-design of the these materials;
- Building up the theory and methodology of green tribology.

Consequently, tribologists should devote all their efforts to the investigation, application and development of green tribology, thereby making a valuable contribution to the existence and development of humanity.

4. "Zero-wear" effect: selective transfer

It seems expedient, at least briefly, to consider how the achievements that were obtained in the study of self-organizing tribo-systems, and in particular, the "zero-wear" (effect of wearlessness/effect of selective transfer—ST), play a role in the circle of tasks which green tribology is designed to solve.

The effect of ST in friction was registered as opening in 1966, with a priority in 1956. The authors of this discovery – D.N. Garkunov and I.V. Kragelsky – stated that the essence of the observed phenomenon as follows: "…that in the friction of couple copper alloys-steel under boundary lubrication, eliminating the oxidation of copper, there is a phenomenon of ST of a solid solution of copper from copper-alloy to steel and its transfer backwards from steel to copper alloy, with a reduction of the friction coefficient as liquid lubrication and leads to a significant reduction in wear of the friction pair…" [4].

In the closing years of the XX century the "zero-wear" effect is defined as one of the examples of self-organization in frictional interaction in tribological systems [41, 42], and since then, a synergistic approach at his description has become essential.

Classical tribo-system for realizing of ST is a system of "copper alloy (bronze or brass) – aqueous or alcoholic solution of glycerol – steel". The evolution of the tribological properties of this system visually demonstrated the self-organization in friction in ST mode, which is expressed in the ultra-low frequency vibrations of the friction coefficient and of the size of the rubbing bodies (**Figure 6** [42]).

Self-organization in the ST mode during friction is the consequence of the complex tribo-chemical reactions and physico-chemical processes occurred in the area of frictional contact, which lead to the manifestation of unique tribological characteristics: super-antifrictional (friction coefficient ~ 10^{-3}) and without wear (intensity wear ~10^{-15}). This condition of tribo-system was provided by a protective nanocrystalline servovite film made of soft metal with unusual combination of mechanical properties [43]. According to the results of nanoindentation, such a film has "super-hardness" at compression and "super-fluidity" at shear [44].

Within the framework of the I.V. Kragelsky's molecular-mechanical theory, the providing extremely low friction coefficients and practical absence of wear during friction of solids is possible either at spontaneous generation of wear auto-compensation systems or in the case of friction of perfectly smooth two-dimensional crystals, in which show up only molecular component of the friction force that occurs, such as, during friction of graphene [45].

In the engineering practice, the auto-compensation systems of wear during friction in the ST regime, usually are formed by selecting (a) the materials of tribo-coupling, (b) a composition of lubricants, and (c) a construction of the friction units. As a result of successful material science and engineering solutions, tribosystems are capable of self-organization, in which the process of frictional interaction

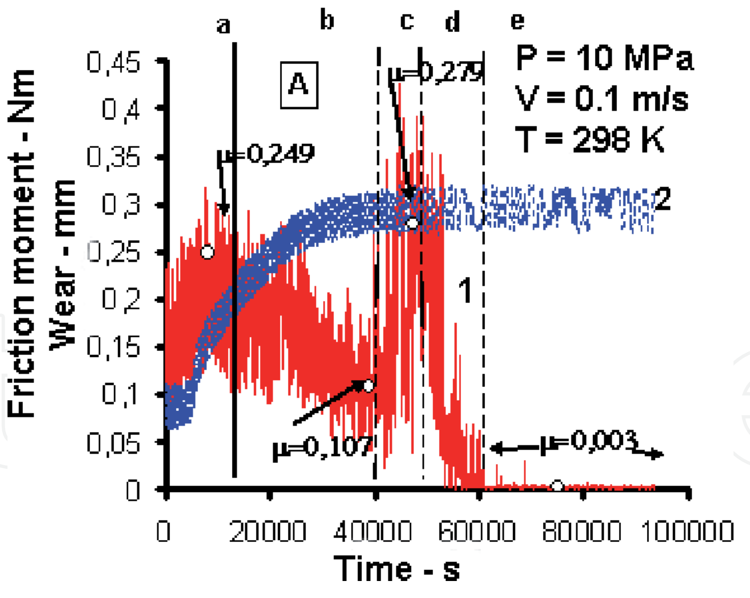

Figure 6.
The evolution of the tribological properties (1 – friction moment, 2 – the linear wear) in tribo-system brass-glycerol-steel. A (a, b) – running-in; c, d – transition mode; and e – the ST mode [42].

moved to the nanocrystalline quasi-liquid [3], and thus provides the friction coefficient, which is characterized for hydrodynamic friction, forming nanoclusters with almost perfect crystals, that leads to increases in load capacity and wear resistance of the friction surfaces.

In practice, "zero-wear" functioning of friction is achieved most often by application of metal-plating lubricants in the real friction units: oils, plastic lubricant, self-lubricating materials and coatings [3].

The mechanism of "zero-wear" effect during friction does not follow from the existing theoretical conclusions about the nature of the frictional interaction. Therefore, none of the attempts to propose developed in detail and experimentally substantiated scientific approach to explaining the "zero-wear" effect is currently generally recognized, although works aimed at clarifying the causes of friction without wear have been underway for more than half a century, during which reliable experimental facts have been accumulated and consistent approaches have been proposed that allowed to qualitatively explain the evolution of the tribotechnical characteristics of friction pairs during realization of the ST.

Currently, it has been reliably established that the composition, thickness and properties of servovite film during frictional interaction continuously change so that the extrapolated to the infinity friction surface is a pure copper (**Figure** 7), whose stability during friction is provided by the absorption of surfactants from the lubricating medium [42, 46].

Detailed studies on tribochemical reactions, as well as the evolution of the chemical composition of the servovite film on friction surfaces in the "zero-wear" regime, made it possible to characterize in detail the products arising during friction and to establish their role in the mechanisms of formation of boundary layers during self-organization of not only the classical tribosystem "copper-glycerin-steel", but also a number of more effective tribosystems using other lubricants, such as aqueous solutions of polyhydric alcohols, solutions of sucrose, glucose, galactose and other carbohydrates [3].

String of sequential and parallel chemical reactions: tribo-oxidation, tribo-coordination, tribo-restoration, tribo-reducing decay of coordination compounds, tribo-polymerization, tribo-clusterization and others, etc., accompanying, and/or generating vibrational tribo-chemical reaction, vibrational electrical and

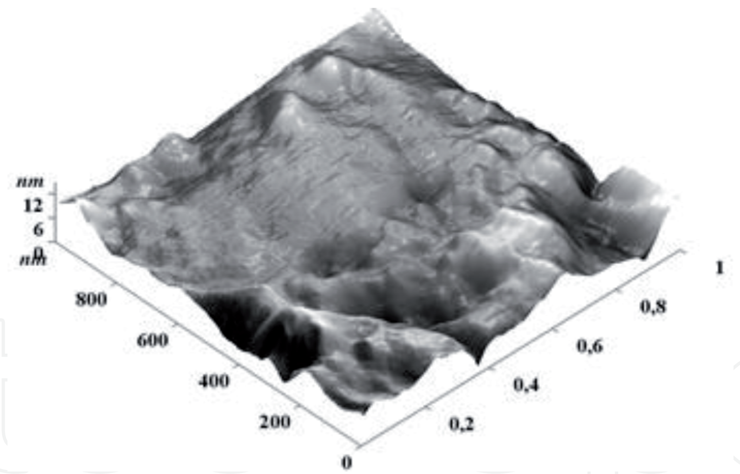

Figure 7.
AFM (3D-visualization) of the surface of the servovite transfer film (brass on steel in glycerol) [42].

electrochemical effects, vibration of the size of rubbing bodies and tribological characteristics of friction pairs - that's the one, is far from complete.

In the most general case, the evolution of the open tribo-system "copper alloy-glycerin-steel", classical for the realization of the "zero-wear" effect, from the thermodynamically equilibrium state of rest under constant external initial conditions (P, V, T) to the friction regime without wear always starts with high (more than 0.1) values of the friction coefficient and large running-in wear, which leads to an increase in the energy intensity of the frictional contact zone and triggers complex physicochemical transformations in the lubricating medium and on the contacting surfaces of copper alloy and steel. At the same time, in the initial period of time, the friction of the copper alloy against steel in glycerin does not differ in nature from the boundary friction, which manifests itself both in the tribo-technical, electrical and electrochemical contact characteristics. The products of wear accumulating at this time in glycerin have a very wide particle size distribution from 10^{-7} to 10^{-3} m and are almost exclusively particles softer from contact bodies of copper alloy. Wear, repeatedly increasing surfaces of copper alloy in the tribo-system, leads to the predominant role of topochemical and tribo-chemical effects, both in the lubricant composition and on the friction surfaces, which reflect in the tribo- and topochemical oxidation of glycerin with the accumulation of a wide range of oxygen-containing surfactants (aldehydes, ketones, carboxylic acids, ethers and esters, as well as oligomeric and polymeric products of their further transformations). Parallel to this, the formation of complex compounds (tribo-coordination) occurs both on the surface of wear particles and on the friction surfaces, and the soluble coordination metal compounds accumulate in the solution [3, 47–49].

Leading of tribo-chemical mechanisms on electrochemical reasons on the friction surface and on the surface of wear of particles is oxidation of copper $Cu^0 - 2e = Cu^{+2}$ (in the case of bronze) or zinc $Zn^0 - 2e = Zn^{+2}$ (in the case of brass) in result of its selective dissolution. Other metals that are part of the friction alloys such as Fe, Sn, Pb, etc., are also subjected to tribo-oxidation with the formation of metal-containing products, so that in the lubricating medium and on the frictional surface simultaneously there is a wide gamma of products, in which the explicitly pronounced tendency in the initial period is the accumulation of oxidized forms of different metals and oxidation products of the lubricant. An important event at this stage of evolution is the accumulation in the lubricating medium and reducing the size of the metallic wear particles with a simultaneous change in their composition due to above reasons. This leads ultimately to the accumulation of metal-containing products upto critical concentrations and thus, to the change of lubricant composition in becoming a metal-plating lubricant. There is a radical change of physico-chemical, electrochemical and tribological situation on the friction surfaces and in the zone of frictional contact. Tribo-system in the course of long enough evolution (in the laboratory it is about 10^3 m of sliding distance) reaches the bifurcation point with transition either to "zero-wear" friction regime or to the regime of the catastrophic wear.

In the transition and functioning of the tribo-system under ST, both contacting surfaces in friction as copper alloy and steel have the same composition and structure. This is another paradox of ST and an unusual combination of materials of the rubbing surfaces. It has been observed that during friction of the same materials (usually in the friction units dissimilar metals and alloys are combined) record-breaking parameters of frictional interaction can be achieved, wherein the self-organization of frictional systems was achieved by the special structure of surface layers.

In the transition from boundary friction to "zero-wear" friction, due to the non-equilibrium character of the processes occurring in the tribo-system (since the system is far enough from the position of thermodynamic equilibrium), and their description by systems of nonlinear differential equations, oscillatory mechanisms begin to appear, which associated with both tribo-chemical transformations in the contact zone, for example, with fluctuations in the concentration of copper-containing products in the lubricant, and with the electrical, electrochemical and tribological characteristics of the contact (**Figure 8**) [50]. Observing this type of oscillations, which always accompany friction in the "zero-wear" regime, prove the manifestation of the self-organization in friction, as well as the transition and functioning of the tribological system in one of the stationary states.

The transient regime from boundary to "zero-wear" friction lasts significantly less than the boundary friction regime, but at this time there are main events that lead to the unique tribological characteristics of tribo-system. It is in this transition that the ordering process occurs, which associated with the formation of a servovite film on the friction surface. The servovite film is formed under nonequilibrium, non-isothermal and topographically unequal conditions, which leads to inevitable differences in its composition and properties in different places of frictional contact. Nevertheless, formation of the film is always due to mutually complementary

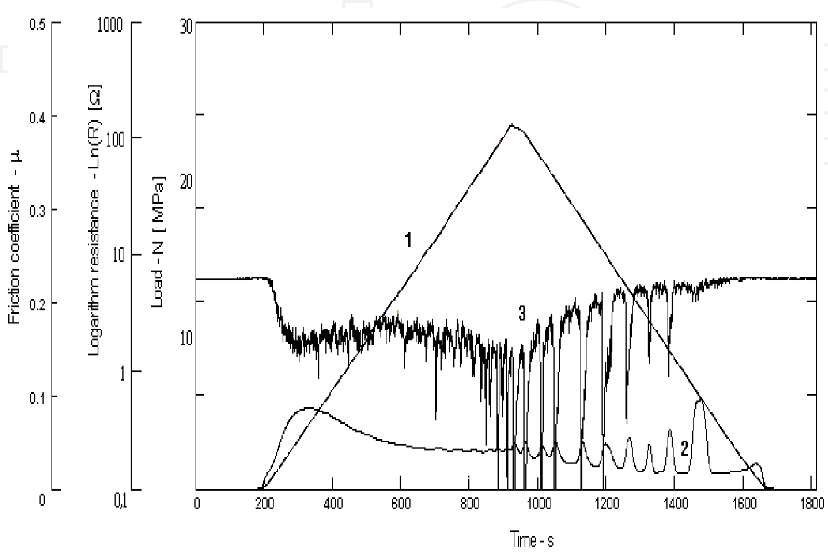

Figure 8.
Fluctuations in the transient regime of "boundary friction – ST" in the friction pair "AISI 1045 Steel–AISI 1045 Steel" in the lubricant of copper nanocluster in glycerol. 1 – load; 2 – friction coefficient; 3 – electrical resistance of contact [50].

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processes of tribo- and electrochemical reduction of coordination compounds of soft metals on the friction surface, clustering their reduced forms, and optimization depending on the friction regimes (P, V, T), sizes (in the nanoscale) and the shape (triaxial ellipsoid) of the clusters in two ways "top-down" and "bottom-up" followed by the direct deposition of metal nanoclusters on the contact surfaces due to tribo-electrochemical effects. The formation of servovite film begins on the individual most active sections of the steel surface, which leads to reducing the friction coefficient and a decrease in the energy density the friction unit. Finally, it is accompanied by a decrease in wear and a transfer of the film formation process to less activated areas on the frictional contact surfaces.

Any system thermodynamically approaches to one of many possible stationary states, the choice of which is caused solely by the initial conditions. It should be noted that the trajectory of the tribo-system during evolution into the "zero-wear" regime is always strictly individual and can never be reproduced in detail. If the tribo-system self-organizes, which in the thermodynamic description is characterized by an increase in entropy and ordering, then its tribological and physicochemical characteristics in a stationary state become almost unchanged (**Figure 9**) [50].

This is due to the fact that a servovite film, formed from individual atoms and their small clusters, has a nanocrystalline structure and, on the one hand, is superstrong in compression, since its nanoparticles are fragments of almost ideal crystals, and on the other hand, the film is quasi-liquid and superplastic under tension and shear due to much weaker interactions between nanoparticles than between atoms in the metal crystal lattice [43].

In this regime, the system can function until continuously accumulating external disturbances or changing external conditions transfer it to a new stationary state, which may be characterized by other and not necessarily higher tribo-technical characteristics, which makes the practical implementation of "zero-wear" in real machines and mechanisms very complex and not always justified event.

At the same time, even with a partial realization of "zero-wear" friction, the effects can be impressive, since when functioning under self-organization conditions and with a slight change in external conditions, the transition to a nearby stationary state is accompanied, as a rule, by a slight change in the tribo-technical properties of the system.

Thus, the application of "zero-wear" effect in engineering practice opens a real opportunity for the design of friction units with significantly increased durability and ultra-high efficiency in terms of friction losses in moving machine interfaces. The "zero-wear" effect in the friction fully fits into the presentation and concepts of

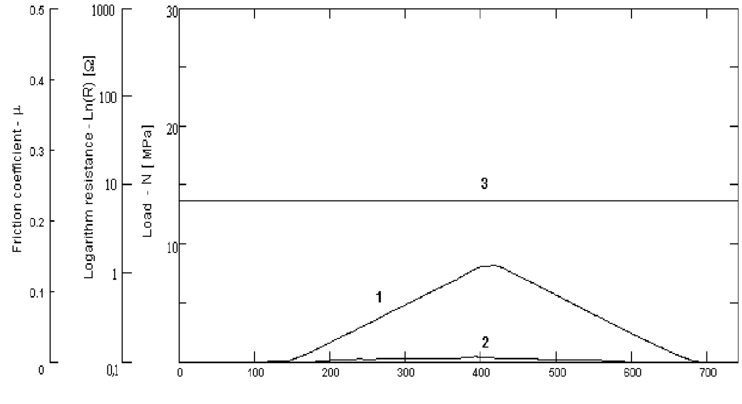

Figure 9.
Stationary regime in the realization of ST in friction pair "AISI 1045 Steel–AISI 1045 Steel" with lubricant of copper nanocluster in glycerol. 1 – load, 2 – friction coefficient, 3 – electrical resistance of contact [50].

green tribology and should be considered as the real embodiment in the theory and practice of modern engineering.

5. Conclusion

Green tribology is a novel area of science and technology. It is related to other areas of tribology as well as other "green" disciplines, namely, green engineering and green chemistry. In this chapter the main scientific and technological aspects of green tribology such as the concept, role and goal, principles, focus areas, challenges, "zero-wear" effect were considered in details.

The concept, role and goal of green tribology were clarified. Green tribology can be defined as an interdisciplinary field attributed to the broad induction of various concepts such as energy, materials science, green lubrication, and environmental science. The goal and essence of green tribology is to save material resources, improve energy efficiency, decrease emissions, shock absorption, investigate and apply novel natural bio- and eco-lubricants as well as to reduce the harmful effects of technical systems on the environment, and consequently, improve the quality of human life.

The twelve principles and three areas of green tribology were analyzed. Observation of these principles can greatly reduce the environmental impact of tribological processes, assist economic development and, consequently, improve the quality of life. The integration of these areas remains the major challenge of green tribology and defines the future directions of research in this field.

Within the framework of this work, one of the most important tribological effects, which is exclusively the basis for green tribology - the "zero-wear" effect in friction (selective transfer effect) was discussed.

As a result, this work allows us to conclude that green tribology is an environmentally friendly and energy-saving concept and, moreover, there are many opportunities for its inclusion in a sustainable society on a global scale. Furthermore, there is a need for tribologists to collaborate towards the development and application of Green tribology.

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Conflict of interest

The authors declare that there is no conflict of interest.

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