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PROPERTIES OF THE BOUNDARY LAYER AND CONDITIONS OF ITS DEVELOPMENT

Boundary layer phenomena are related to adsorption on a friction surface of lubricant particles which can be generally characterized as electrically unneutral, i.e. ions of polar molecules or of electrically charged molecules. Electrically unneutral particles generally occur in lubricants, but they are also generated in the process of friction due to cracking of hydrocarbon chains, electrification and ionization of molecules. The energy of these molecules, in particular those generated in the process of friction, is different and has influence on thickness of the boundary layer, and thereby on friction. The boundary layer made of such molecules can be controlled by electrical, electromagnetic fields. Friction and thickness of the boundary layer can also be controlled. An interesting issue is the range of parameters in which boundary layers are present and determine the process of friction in isolation, thus making it a separate type of boundary friction. This paper show how boundary layers evolve and under impact of what parameters. This allows for informed use of the interesting properties of these layers in practice, and even for control of the friction process.

INTRODUCTION

We assume triboelectric phenomena occur across the entire range of friction conditions, beginning with hydrodynamic friction and ending with wear, though with varying intensity, the latter deciding whether a type of liquid or boundary friction occurs (for instance, triboelectric phenomena have little effect on the friction process in the case of hydrodynamic friction).

An analysis of triboelectric phenomena should take into account problems of the boundary value as the latter consists of oil particles of a greater energy, saturated in contact with a friction surface.

Increased concentration of polar compounds and particles near friction surfaces has already been discussed by B.J. Kostecki [1], T. Stolarski [2].

1. BOUNDARY LAYER

Issues linking surface energy and energy of particles constituting the boundary film are highlighted in descriptions and interpretations of the boundary film.

Let us quote the definition of the boundary layer by [3]: boundary layer (boundary film) is an ordered, several-particle-thick lubricant layer within reach of unsaturated forces of a lubricated surface. The field of these forces induces polarisation of lubricant particles and the associated orientation in parallel to lines of these forces. Viscosity and density of the lubricant superficial layer change as a result. In effect, properties of a lubricant are different in the superficial layer than in the remaining volume. Lubricants containing polar surfactants, such as sulphur and its compounds or aromatic hydrocarbons, are capable of building boundary layers. This capacity is also dependent on energy state of a lubricated surface.

We intend to supplement the foregoing definition with issues that we believe to be crucial: Lubricants containing polar surfactants, such as sulphur and its compounds or aromatic hydrocarbons, are capable of building boundary layers, but this is not all: we claim the energy generated in the friction process electrifies some particles and causes cracking of some hydrocarbon chains, and some electrically unneutral particles are spontaneously produced in this way. These particles may become parts of the boundary layer or create triboelectric phenomena. We take the electrically unneutral particles to mean polar, electrified and ionised particles.

Importantly, in our view, boundary layers defined in this manner are static because they are bound to a friction surface, while the friction process takes place not in but by destruction of these layers. As we know, destruction of static structures involves supply of additional energy, and the closer it is to the surface, the more energy friction requires to overcome the surface energy. Thus, the internal friction on the surface of a superficial layer occurs in a layer potentially containing particles of a static boundary layer being destroyed, which already form part of a dynamic structure subject to another type of ordering. Particles ordered as part of a static boundary layer become disorderly when moving into dynamic structures and begin to be involved in dynamic triboelectric phenomena since electrically unneutral particles are present in the static layer.

In light of the foregoing discussion, we propose the following definition of the boundary layer for purposes of this article:

A lubricant exhibits different rheological properties in a dynamic boundary layer than in the lubricant volume and arises from electrically unneutral particles adsorbed into a friction surface and from electrically unneutral particles produced in the friction area.

In this light, layers of oxides, chlorides, sulphides and other compounds, such as soaps, generated on a surface by action of antiwear additives, are layers of a modified surface and parts of such a surface. They are not boundary layers, therefore. These modified layers are parts of a broader concept discussed in the literature [4] as the operating surface layer (OSL) and can only affect the energetic state of a surface and thus influence boundary layers.

We argue triboelectric phenomena appear in and concern static and dynamic boundary layers, where internal fiction occurs involving electrically unneutral particles. Processes of internal friction in a lubricant layer are always connected with triboelectric phenomena (generation and effect of polar, electrified and ionised particles), yet their intensity depends on friction parameters: the more difficult the conditions (higher speeds, greater unit pressures, higher temperatures), the more intensive the triboelectric phenomena (up to a certain limit of parameters characterising the range of boundary friction).

Intensity of these phenomena may be non-linear, though we are interested in a certain state of saturation with what we will refer to as intensive triboelectric phenomena, demonstrated by the ability to affect the process of friction with electric current and by increased friction (friction coefficient which is markedly greater than in liquid friction and thickness of the oil film that is distinctly greater than within the range of hydrodynamic friction).

Our observations of a dramatic fall of oil film resistance and a concurrent growth of the film's thickness point to the following conclusions:

- the growth of the oil film's thickness combined with a declining resistance of the same film (and a linear rise of the unit pressure) are proof of a restructuring of the friction layer and emergence of electrically unneutral particles in numbers sufficient for electric current to flow through this area as if through a conductor,
- the rising conductivity and appearance of large quantities of electrically unneutral particles relate to increasingly difficult conditions of friction (higher unit pressure in the friction area),
- the growth of the oil film's thickness (despite the linear rise of the unit pressure) is caused by a chaos of disorderly electrically unneutral particles which interact with each other in the friction area.

2. CREATION of a dynamic boundary layer

Symptoms of intensive triboelectric phenomena appear at the time of lubrication with non-polar paraffin oil, thus electrically unneutral particles arise in the friction process under beneficial conditions.

This is illustrated in Figure 1.

We consider conditions of friction with intensive triboelectric phenomena to be the range where a linear growth of unit pressure is accompanied by a declining resistance of the oil film. This is associated with rising thickness of the film and increasing friction, also shown in the above figure.

Our observation is corroborated by the fact that the process of friction could be impacted with electric current (Fig. 2) within the range of conditions giving rise to intensive triboelectric phenomena (stage III, Fig. 1).

The possibilities of influencing the friction process by means of

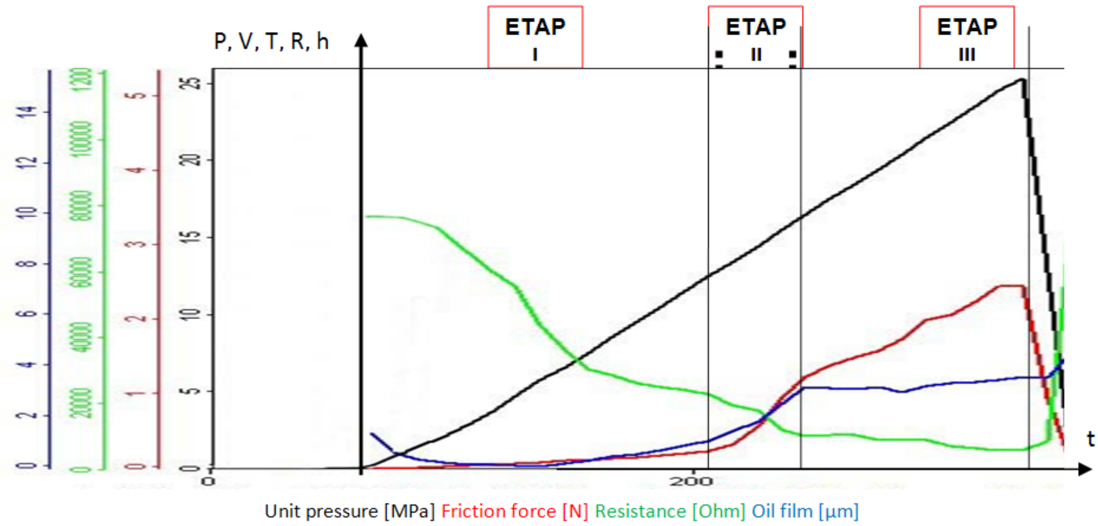

Fig.1. *An illustration of the gradual transfer to intensive triboelectric phenomena: stage I – absence of triboelectric phenomena (hydrodynamic friction), stage II – conditions of transfer to intensive triboelectric phenomena, stage III – presence of intensive triboelectric phenomena*

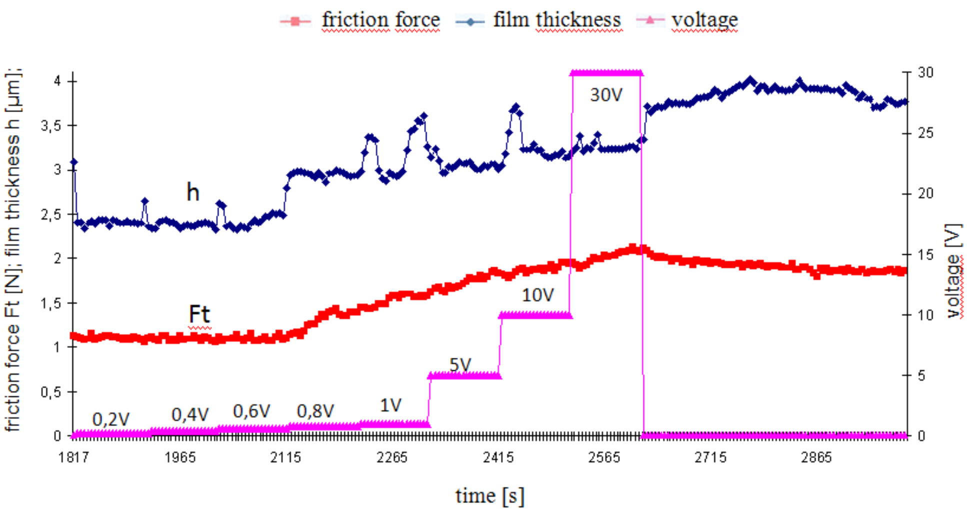

Fig.2. *Effect of electric current on the friction force – measurement of friction force with a friction area affected by the current. Experimental parameters: v=1[m/s], T=40[ºC], p=25[MPa], lubricant – paraffin oil, voltage applied to friction surfaces 0-30 [V].*

electric current shown in Figure 2 suggest that electrically unneutral particles prevail in the friction area and it is these particles that are affected by the current. When electric current is applied to the friction area at stage I, it has no visible effect, which means that even if electrically unneutral particles have already been generated there (e.g. in effect of electrification), their quantity is too low to affect the process of friction in any significant way.

Stage II, separated in Fig. 1, illustrates the range of friction conditions under which the transfer to intensive triboelectric phenomena is effected (triboelectric phenomena decide macroscopic effects of friction). It must be noted this is not an abrupt process.

3. CONSTITUTION OF THE BOUNDARY LAYER

A boundary layer adsorbed into a surface is ordered under impact of energy of a friction surface. This ordering produces high resistance of the layer.

The figure above shows that the increasing film thickness at the time of the oil addition relates to a reduction of the friction force. Interestingly, these are not discrete phases and are proof that a boundary layer constitutes itself (after a certain time). Nature of this constituting is unknown at this stage. It can be only supposed that energy saturation (adsorption) into surfaces of lubricant particles requires some time for electrically unneutral particles to arise from the non-polar paraffin oil in the friction area, which is suggested by a slow decline of the friction force and a gradual increment of the film thickness.

The issue of the slow constitution of the boundary film (ordering of particles) is illustrated by the resistance recorded in Figure 3, where resistance commences to grow after a considerable delay and the growth is smooth compared to changes of the friction force and of the oil film thickness.

This slow increase of resistance shows that restructuring of the boundary film into an orderly state characterised by a high resistance is slow and that electrically unneutral particles are ordered, which display an excellent conductance of electric current that reduces as the particles are arranged appropriately. It can be stressed at this point that an unordered boundary film has properties of a good conductor. This can be generalised into a hypothesis that disorderly and electrically unneutral oil particles (which can be expected to accumulate near the surface) are capable of conducting current.

Fig. 3 implies electrical resistance (in the range of boundary friction) is unrelated to thickness of the boundary film, while a constituted (ordered) boundary film is characterised by high resistance. It can be surmised, therefore, that, within this range, electric resistance in the friction area is a key characteristic of the area's structure.

Continuing our programme of research, we loaded the friction

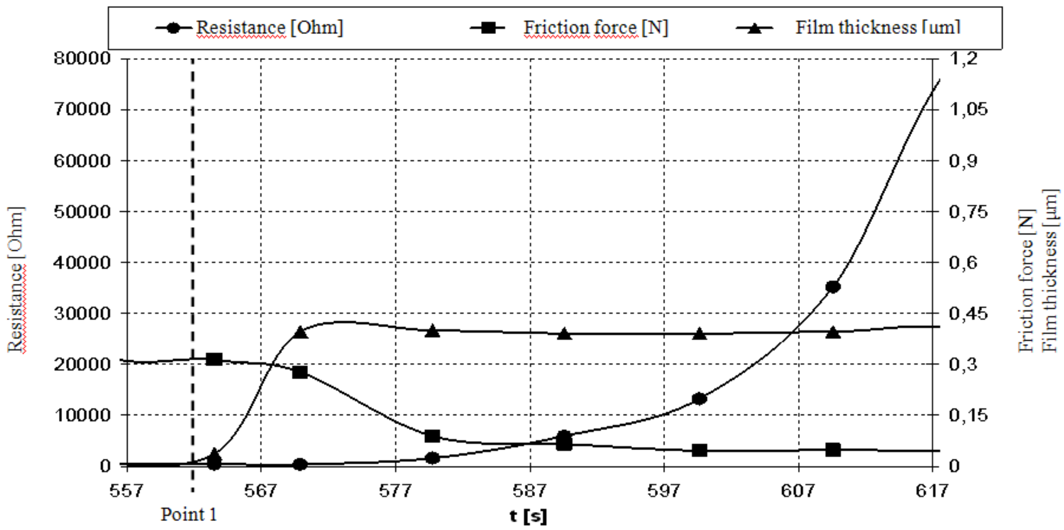

Fig. 3. Illustration of triboelectric phenomena of boundary oil film generation. Point 1- the instant at which the lubricant (paraffin oil) is added.

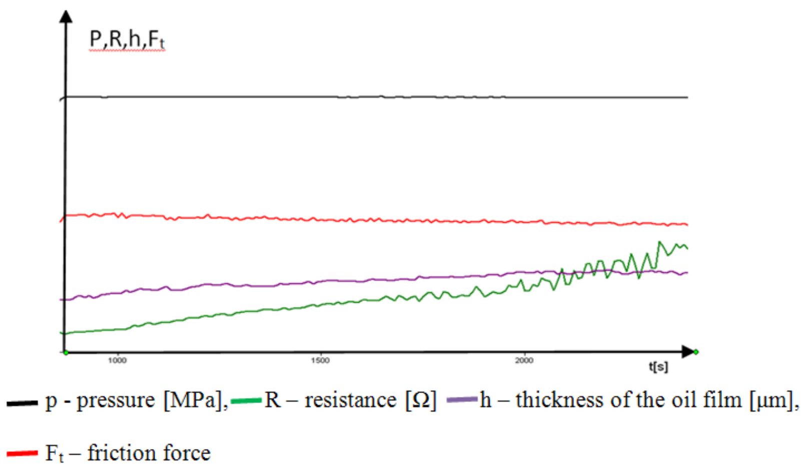

Fig. 4. Constitution of a boundary layer over time. Experimental parameters: v=1[m/s], T=40[°C], p=30 [MPa], lubricant – paraffin oil.

area with linearly rising unit pressures until the boundary film began changing its tribological properties. Escalation of the unit pressures was discontinued and they were maintained at steady levels in order to determine how the stabilised conditions affect restructuring of the boundary zone over time. This is illustrated in Figure 4.

The increasing friction force suggests the nature of the newly-constituted structure of the dynamic film and indicates its disorderly state. It is very important to point out growth of resistance across the oil film is related to restructuring (let us recall and emphasise that the slow restructuring is caused by displacement of low-energy by high-energy particles generated in the dynamic area) of the orderly boundary layer, which exhibits poor conductance.

This leads to the following conclusion: the friction process occurs on the border of the ordered (static) boundary layer and the layer of intensive triboelectric phenomena (dynamic boundary layer) while friction resistances depend on the distance from this layer to the friction surface. The following important fact must be stressed: high energy particles produced in the sliding area are incorporated into the boundary layer and slowly increase its thickness and durability while reducing friction, which probably relates to the greater distance from the friction surface and ordering of lubricant structures in the friction area. It must be underlined once again that reinforcement and constitution of the surface boundary layer is related to displacement of lower-energy particles, fixed in the surface layer by forces of the unsaturated boundary surface energy, with high-energy electrically unneutral particles generated by the process of friction.

This is demonstrated in Figure 4, where a resistance rise, a slight increment of the oil film's summary thickness and a slow decline of the friction force can be observed.

Conclusions from Figure 4 suggest that the real friction area (on the border of the static boundary layer and dynamic triboelectric layers) generates energy which contributes to creation of the triboelectric layers. That is not all, however: highly energised particles produced in the sliding area are incorporated into the boundary layer, restructuring it and thereby making it thicker and more durable.

Figures 4 and 6 show an experiment carried out under stabilised conditions of pressure, temperature and velocity, though over a relatively long period. It can be noted that resistance of the friction zone slowly rises whereas the friction force declines a little.

In order to illustrate the foregoing concept of boundary layer constitution and entrenchment over prolonged durations of triboelectric phenomena in stabilised conditions, let us employ a model of friction area described in [9] and shown in Figure 5.

This model serves to explain that the static boundary layer and the dynamic boundary layer, where intensive triboelectric phenomena take place, consist of identical, electrically unneutral oil particles, the difference being that the superficial (static) boundary layer is ordered by forces of surface energy whereas the boundary triboelectric (dynamic) layers are disorderly.

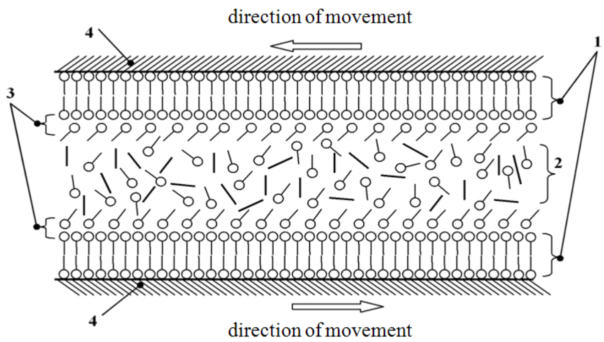

***Fig. 5.** Model of a static and dynamic boundary layer in the process of friction: 1 - static boundary layer; 2- triboelectric (dynamic boundary) layer; 3 - sliding areas; 4 - surfaces in friction.*

The increasing resistance indicates that thickness of the (orderly) boundary layer rises. This can be explained by rebuilding of the boundary layer through a selective incorporation of particles of an appropriately high energy, with the boundary layer becoming thicker and more durable owing to improved ordering. The hypothesis that this is a result of improved ordering is suggested by the fact that the ordering effects of the boundary layer or disruption of this order that we observe continue for relatively long times, which characterises processes of boundary layer constitution exhibiting growth of electric resistance.

In order to provide one more confirmation that constitution of the boundary layer (ordering of structures) is slow, the following experiment was carried out: a 1.1 [V] electric current was applied and caused damage to the boundary layer. The friction coefficient rose markedly on such application of current, though it took 25 [s], as shown in Figure 7.

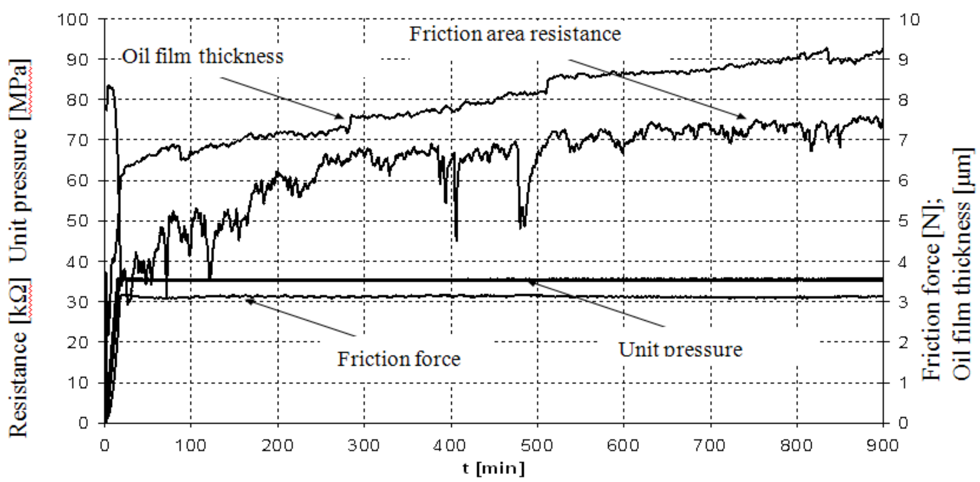

***Fig.6.** Illustration of growth of the boundary film thickness caused by duration of testing*

Removal of the current from the friction area caused friction coefficient to diminish but restoration (natural – without outside intervention) of the boundary layer properties occurs after a very long time - approx. 300 [s]. This is illustrated by Figure 8 [10].

Other factors influencing and increasing the resistance to tribological wear have been investigated in [11].

CONCLUSIONS

1. Testing of the boundary layer in dynamic conditions brings new information about its properties.
2. Static boundary layers are composed of unneutral lubricant particles which occur in the lubricant naturally, but also of electrically unneutral particles generated in the friction process.
3. Process of friction generates powerful triboelectric phenomena which in turn act on the structure, thickness and properties of the summary (static and dynamic) boundary layer.
4. Exploration and understanding of processes and conditions of occurrence of static and dynamic boundary layers will allow for their informed application in practice.

REFERENCES

1. Kostecki B.J., Natanson M.E., Bierszadski L.I., *Mechano-chemiczne procesy przy tarciu granicznym*, Nauka, Moskwa 1972.
2. Stolarski T., *Zjawiska mechano-chemiczne towarzyszące tarciu łożyska ślizgowego smarowanego mieszaniną smaru ŁT4 i policzterofluoroetylenu*, Inżynieria łożyskowania, Politechnika Gdańska 1976.
3. Szczerek M., Wiśniewski M., *Tribologia, tribotechnika*, PTT 2000.
4. Marczak R., *Fizykochemia procesu tarcia*,Tribologia, t. 5, 2000.
5. Krawczyk K., Firkowski A., Nowiński E., Chojnacka A., Stępniewski M., Polit W., Klasek T., *Ocena zmian grubości filmu olejowego w badaniach tribologicznych*, Zeszyty Naukowe Instytutu Pojazdów PW nr 2/2010.
6. Kajdas C., Krawczyk K., Nita J., *Method and device for testing lubricating properties of lubricating means*, U.S. Patent No. 4311036, 1981.
7. Kajdas C., Krawczyk K., Nita J., *Sposób i układ do pomiaru własności smarnych środków smarowych*, Patent polski nr p202886, 1980.

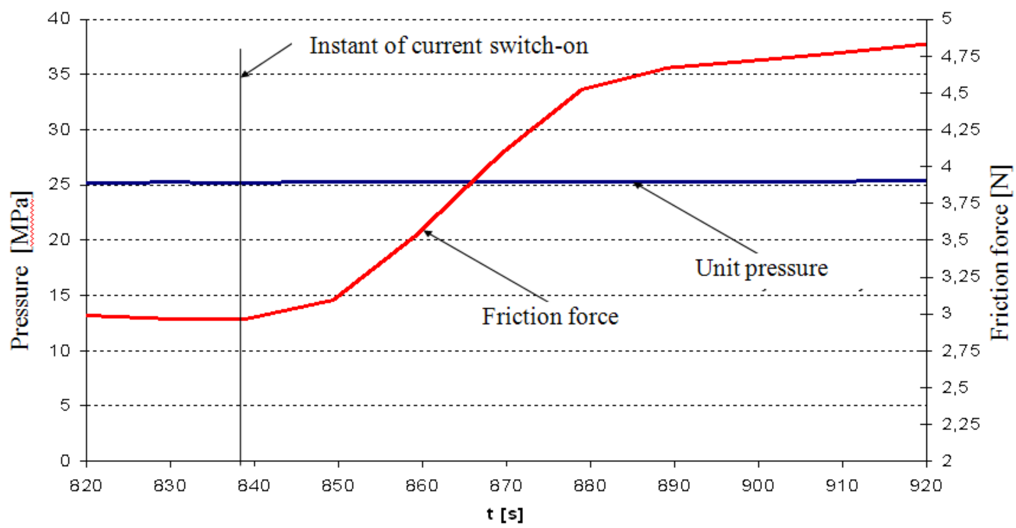

Fig. 7. *Variation of the friction force effected by switching-on of electric current. Experimental parameters v=0.5[m/s], T=40[ºC], p=25 [MPa], lubricant – paraffin oil*

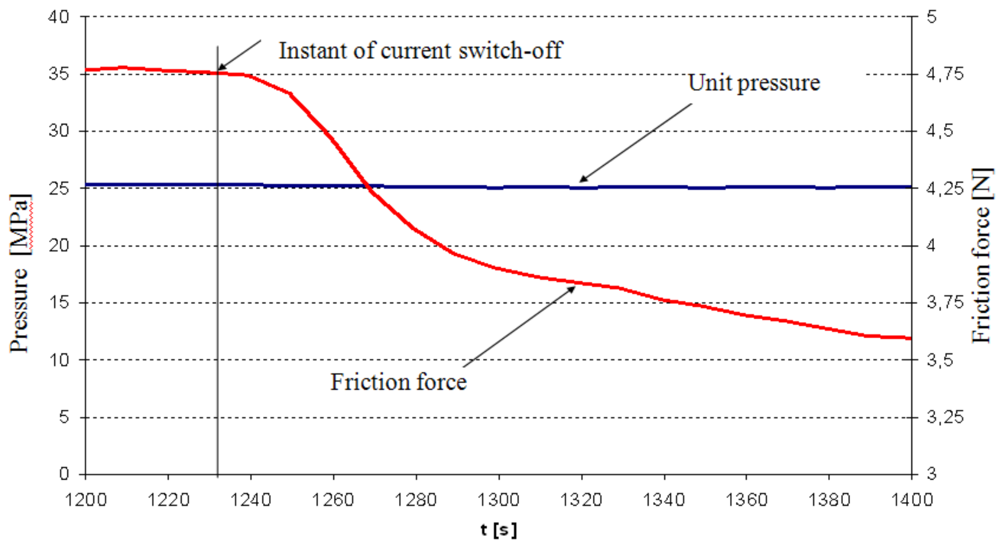

Fig. 8. *Variation of the friction force effected by switching-off of electric current. Experimental parameters V=0.5[m/s], T=40[ºC], P=25 [MPa], lubricant – paraffin oil [10]*

8. Kajdas C., Krawczyk K., Nita J., *Metode und Gerät für Berstimung fürtribologichen Eigenschaften von Schmierstoffen*, German Patent No. G-7364644, 1981.
9. Krawczyk K., *Zjawiska triboelektryczne w warstewce rozdzielającej powierzchnie trące podczas tarcia ślizgowego*, Zeszyty Naukowe Instytutu Pojazdów PW nr 2/2010.
10. Żurowski W., Krawczyk K., Nowiński E., Wronka G.: *Conditions of development of the boundary layer and some of its properties* in TRIBOLOGY 2015 (ed. P. de Vaal). SAIT, Pretoria 2015.
11. Żurowski W., *Structural factors contributing to increased wear resistance of steel friction couples,* Eksploatacja i Niezawodność - Maintenance and Reliability, 2012 Vol. 14, No. 1 19-23.

Właściwości warstwy granicznej i warunki jej występowania

Warstwy graniczne związane są ze zjawiskami adsorpcji na powierzchni trącej cząsteczek środka smarowego ogólnie scharakteryzowanych tym, że są nieobojętne elektrycznie, czyli jonów cząsteczek polarnych i cząsteczek naelektryzowanych. Cząsteczki nieobojętne elektrycznie na ogół występują w sposób naturalny w środkach smarowych, ale też powstają w procesie tarcia na skutek pękania łańcuchów węglowodorowych, elektryzacji cząsteczek oraz jonizacji. Energia tych cząsteczek, szczególnie powstających w procesie tarcia jest różna i posiada wpływ na grubość warstwy granicznej, opory tarcia. Warstewką graniczną zbudowana z takich cząsteczek można sterować za pomocą prądu elektrycznego i pól elektromagnetycznych. Sterowaniu podlegają opory tarcia i grubość warstewki. Interesującym problemem jest zakres parametrów, w których warstewki graniczne występują i samodzielnie decydują o procesie tarcia, a więc jest to wydzielony rodzaj tarcia granicznego. W niniejszej pracy pokazano jak ewoluują warstwy graniczne i pod wpływem jakich parametrów. Można w ten sposób świadomie wykorzystywać właściwości tych warstw w praktyce, a nawet sterować procesem tarcia.

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