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Elektrionized[™] Vegetable Oils as Lubricity Components in Metalworking Lubricants

Lubricity additives, also known as friction modifiers, are steadily gaining acceptance from lubrication engineers. The present communication focuses on applications of such additives in formulation of metalworking lubricants, such as straight oils and soluble oils, explaining how such additives function and which parameters control lubricity of finished formulations. It is demonstrated that, unlike extreme pressure additives, which act when a direct asperity-to-asperity contact occurs in the boundary lubrication regime, ionized vegetable oils function by postponing the onset of the boundary lubrication regime.

Keywords: metalworking fluids, lubricity additive, ionized vegetable oil, elektrionization, industrial lubricants.

1. INTRODUCTION

Development and broad commercialization of catalytic hydrotreatment technologies in the period since 1970s to 1990s has created an abundant supply of highly refined base oils. These base stocks have extremely low sulfur content, low volatility and excellent antioxidant response. However, as a result of their saturated chemistry, an important property they lack is lubricity.

The term "lubricity" refers to the slipperiness of lubricant films formed in boundary lubrication, a condition which lies between unlubricated sliding and fluid-film lubrication and which is also defined as a condition in which the friction between the surfaces is determined by the properties of the surfaces and properties of the lubricant other than viscosity. Boundary lubrication encompasses a significant portion of lubrication phenomena in metalworking operations.

The main function of lubricants in tribological systems is to reduce friction and wear. The reduction of friction and wear results from the formation of a lubricant film separating the rubbing surfaces. The thickness of the lubricant film depends upon constituent chemistry (base oil and additives), as well as upon the operating conditions, specifically the applied load and the sliding velocity. At a sufficiently high load lubricant may be expelled from the friction zone, leaving the rubbing surface unlubricated. In this case, severe friction and wear occur.

To alleviate the dramatic effect of "dry" friction, extreme pressure (EP) additives are deployed. Those additives, normally containing sulfur, phosphorus, chlorine or molybdenum derivatives, are capable of reacting with the material of rubbing surfaces to form a thin surface layer of chloride, phosphate or sulfide, which act as a solid lubricant when the rubbing surfaces

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come into a direct surface-to-surface contact with each other. When unlubricated sliding is encountered, friction and material deformation generate enough heat to trigger EP reaction. However, the price of that is a microscopic scar left at the surface. Such scars are accumulated with time to give wear.

Unlike extreme pressure additives, which act when a direct asperity-to-asperity contact occurs in the boundary lubrication regime, lubricity additives – also known as friction modifiers, work by postponing the onset of the boundary lubrication regime as explained in Figure 1.



Figure 1. Tribological effects of extreme pressure additives (EP) and fatty oiliness additives (FM). The Stribeck diagrams plot the logarithm of the coefficient of friction versus the logarithm of the Hersey number

Equivalently, one may talk about expanding the borders of the film lubrication regime: in a loading cycle (when moving from the right to the left over the Stribeck curve), the film lubrication will stay longer and stand higher loads, and in an unloading cycle (moving from the left to the right), the change from boundary lubrication to film lubrication will occur earlier.

A good lubricity additive is expected to combine a sufficiently high surface affinity and the ability to form a sufficiently thick and resilient protective film, as well as the ability to dissolve in base oils where it is meant to be used in. It is also important that the protective film formed does not inhibit reactions of conventional EP additives. Surface adsorptivity normally increases with increasing polarity of the additive, while thickness of the adsorbed film increases with increasing its viscosity (which, in its turn, can be related to increasing average molecular weight). At the same time, excessive polarity and viscosity will undermine miscibility of the additive with hydrocarbon base stocks. In order to reconcile these antagonistic tendencies, an amphiphilic molecular structure (similar to that of surfactants) is to be preferred. Other important factors are thermal stability, oxidation stability, low volatility, as well as ecological and health safety considerations.

The protective layers formed by lubricity additives are self-regenerating: if the layer is damaged by applying too high stress, it will be restored by adsorption of a new portion of friction modifier from the bulk and by lateral diffusion of adsorbed molecules caused by a surface pressure gradient.

The present study deals with the tribological properties of a special class of bio-based lubricity and fatty oiliness additives produced by ElektrionizationTM of vegetable feedstocks. ElektrionizationTM is a proprietary process whereby feedstocks undergo electroionizing treatment which leads to an increase in viscosity, polarity and viscosity index [1,2]. Vegetable oils, in general, have superior lubricity as compared to mineral oils and are often used as lubricity components in lubricant formulations [3,4]. The Elektrionization™ technology builds upon this natural property by addressing some purity and stability concerns. Increasing the polar functionality of the triglyceride molecules of vegetable oil has a positive impact on wear protection, probably due to the stronger adsorption to the metal surface and the stabilization of the adsorbed layer by lateral interlinking [4]. Featuring a unique combination of viscosity and polarity, ionized vegetable oils form sufficiently thick and resilient protective layers by adsorption to rubbing surfaces. Although these additives are successfully applied in various fields of lubrication engineering, the present communication focuses mainly on metalworking applications.

2. EXPERIMENTAL

Tribological tests were carried out using a pad-on-disc tribometer (steel on steel) specially designed to enable friction coefficient measurements accurate in hydrodynamic, elastohydrodynamic and boundary lubrication regimes. The conceptual instrument setup is outlined in Figure 2 and consists of two steel pads pressed against a rotating steel disk immersed in the studied lubricants. The rotation speed and the pressure applied to the plates can be varied, and the resulting torque produced by the friction force measured, whereby the coefficient of friction is derived as a function of the Hersey number (viscosity \times sliding velocity / applied pressure). Testing results were presented in the form of Stribeck diagrams plotting friction coefficient versus Hersey number.



1 – Mounting plate; 2 – Container filled with oil; 3 – Rotating metal disk; 4 – Metal pads pressed against the disk; 5 – Rods for applying pressure to the pads; 6 – Flexspring for controlling torque; 7 – Laser-based optical sensor for measuring angular deviation

Figure 2. Scheme of the tribometer used for Stribeck curve measurement

The Hersey value has a unit of length and may be considered as a measure of effective lubricant film thickness between the rubbing surfaces. The use of Stribeck plots allows a compact and consistent representation of data collected at various loads and sliding velocities. The actual pressure settings were 1.96, 3.92, 5.89, 7.85 and 9.81 bar. The test conditions were adjusted so as to cover the transition from the elastohydrodynamic (EHD) to the boundary lubrication regime.

Some typical properties of the lubricants used in the tests are summarized in Tables 1, 2 and 3.

Table 1. Properties of E-ION R lubricity additive (E	-ION s.a.,
Belgium)	

Property	ASTM	Unit	Value
Viscosity at 40 °C	D445	mm ² /s	2300
Density at 15 °C	D1298	g/cm ³	0.91
Viscosity index	D2270	-	270
Sap. number	D94	mgKOH/g	89
Aniline point	D611	°C	85
Pour point	D97	°C	- 3
Flash point	D93	°C	270

Table 2. Properties of mineral oil (100N, Total)

Property	ASTM	Unit	Value
Density at 15 °C	D1298	g/cm ³	0.87
Viscosity at 40 °C	D445	mm ² /s	22.8
Viscosity index	D2270	-	97
Flash point	D93	°C	210
Pour point	D97	°C	- 12
Neutralization number	D974	mgKOH/g	0.03

Temperature	Viscosity [mm ² /s]		
[°C]	without E-ION R	2.5 % E-ION R	10 % E-ION R
30	30.62	34.92	51.77
50	14.12	16.14	24.46
80	6.15	7.00	9.98

Table 3. Viscosity of 100N oil depending on the concentration of the additive and temperature

3. TRIBOLOGY OF ELEKTRIONIZED™ VEGETABLE OILS

3.1 Improving lubricity of mineral base oils

Mineral oils are the most common base oils for formulation of metalworking lubricants. Needless to say that lubricity is one of the most important quality parameters for this lubricant group. Elektrionized[™] vegetable oils significantly improve lubricity of mineral oils. Experiments show that, by increasing the content of lubricity additive E-ION R in 100 N mineral base oil from 0 to 10 %, the Stribeck curve is progressively shifted to the left (Fig. 3). In practical applications, increased lubricity translates into higher processing speeds, reduced consumption of lubricants, better production economy, and reduced environmental load.





3.2 Synergy with conventional EP additives

As explained in Figure 1, the effect of lubricity additives such as E-ION R is limited to Hersey number range in which transition from film lubrication to boundary lubrication occurs. Lubricity additives elevate the threshold pressure at which the dry contact will occur but do not provide protection beyond that point. Therefore, for maximum protection under various tribological scenarios, it is important that EP additives be deployed as well in finished formulations. Wear preventive characteristics of a few model lubricants formulated with ionized vegetable oils and conventional EP additives were compared using the standard four-ball method, see Table 4. These results show that there is a synergetic effect between ionized vegetable oils and EP additives.

The protective surface film formed by E-ION R can be viewed as a sponge impregnated by base oil, which contains EP molecules present in finished formulations. Within the friction contact, when rubbing surfaces are sliding against each other, such a film undergoes very rapid deformations. The heat generated due to friction and strain, in combination with a high pressure, are enough to render EP molecules surface-reactive. As a result, the EP reaction will start before unlubricated contact occurs.

Table 4. Results of four-ball test carried out on 100N mineral oil treated by two common EP additives and E-ION R friction modifier. The test condition were similar to D2266 (75 °C, 1200 rpm, load 50 kg and test duration 1 hour)

Lubricant composition	Average scar diameter [mm]	Observed wear reduction [%]
Pure mineral oil 100N	1.09	0
100N + 1 % tricresyl phosphate	0.74	32
100N + 1 % di-tert-butyl polysulfide (TPS 32)	0.71	35
100N + 1 % tricresyl phosphate + 5 % E-ION R	0.52	52
100N + 1 % di-tert-butyl polysulfide + 5% E-ION R	0.45	59

3.3 Surface cleanliness and sludge control

E-ION additives reveal excellent antisludge activity which can be demonstrated in a simple and instructive experiment: Let's take a mineral oil such as NS8 (naphthenic, Nynas) or 100N (paraffinic, Total), which are quite common in soluble oil formulations, add 10 % E-ION R additive, and leave it to oxidize in an open beaker in an oven at 150 °C for a week or so, together with a sample of unadditivated oil as a reference. Normally, even under so severe oxidizing conditions, no sludge is produced in oil treated with E-ION R – in a sharp contrast to additive-free oil yielding a lot of sludge under the same conditions (Fig. 4). Differences in surface cleanliness observed in field trials are also striking.

Figure 4. Antisludge efficiency of E-ION R in mineral oil (open beaker oxidation test, 150 °C, 5 days)

4. USE OF ELEKTRIONIZED™ VEGETABLE OILS IN SPECIFIC OPERATIONS

ElektrionizedTM vegetable oils are highly efficient as lubricity and oiliness additives in formulation of metalworking lubricants. The usual treatment levels may range from 5 to 15 % in cutting and from 10 to 20 % in forming applications. In the following, a few application examples are discussed.

4.1 Balancing lubricity and cooling efficiency in formulation of cutting lubricants

High stress transferred from the cutting tool to the work piece causes material displacement at the high shear rate, generating a lot of heat. It is estimated that around 75 % of heat generated by various cutting processes is due to material deformation and only 25 % due to friction. This makes cooling efficiency of cutting fluids one of the primary considerations [5]. Since water is a good coolant, due to its high specific heat and heat of vaporization, aqueous emulsions of mineral oils are commonly used as cutting lubricants. In such lubricants, the role of oil is to lubricate and the role of water is to cool.

In cutting operations, high localized stresses always bring some risk of adhesive wear and edges build-up on the tool. There is some distinction between high speed and low speed operations: for low speed machining, there is no excessive heating, and hence, lubrication efficiency of the cutting fluid is the only important consideration. For high speed machining, heat formation in the shear zone becomes a limiting factor. In this case, the importance of lubricity is often overlooked. However, as long as high stresses are still there, a cutting fluid that only cools but does not lubricate will never perform adequately. Poor surface finish, resulting primarily from chip welding, tool seizure and edge build-up, and fatigue and flank face wear of tools are the signs of inadequate lubricating efficiency of cutting fluids.

Figure 5. Common tool failures that may be linked to insufficient lubricity of cutting fluids (top) and the simulated stress distribution in the cutting zone (bottom)

Use of lubricity and fatty oiliness additives produced by $Elektrionization^{TM}$ of vegetable oils allows one to

enhance lubrication efficiency of cutting fluids without increasing the volume fraction of oil in emulsions. These additives also facilitate transportation of swarf and chips from the cutting zone, thus minimizing flank wear, prevent rewelding, stabilize oil against oxidation, reduce misting and extend useful tool life. Due to their low volatility, good high-temperature stability and high lubricity, ElektrionizedTM vegetable oils are an ideal choice for applications designed around the minimum quality lubrication concept.

4.2 Lubricity and runnability of deep-drawing operations

Deep-drawing is an example of metalworking operation where process runnability is controlled both by the extreme pressure properties of metalworking lubricant deployed as well as by its lubricity under moderate pressure corresponding to elastohydrodynamic lubrication regime [5]. The process operation is outlined in the Figure 6. The extreme pressure points are marked by arrows. In those points, EP additives, such as phosphorus and sulfur, are effective. However, the tribological conditions between the work piece (metal blank) and the die top, as well as the conditions between the work piece and the holder correspond to elastohydrodynamic lubrication regime. In this regime, EP additives have no effect. If the lubricating oil has insufficient lubricity, process runnability may be affected. Cup rupture is most common failure associated with a lack of lubricity. Ironically enough, this failure is often associated with an ill-judged attempt to "modernize" the process by switching to pricey base oils produced using severe hydrotreatment. As mentioned in the introduction, one important property the hydrotreated oils lack is lubricity. Use of ElektrionizedTM vegetable oils as lubricity additives will normally remedy the problem without incurring any health or environmental risks.

Arrows mark high stress points

Figure 6. Principle of deep-drawing operations (extremepressure points are marked by arrows)

4.3 Lubricity in wet wire-drawing

Use of high-speed multi-pass wet wire drawing operations is steadily growing due to productivity benefits it offers over traditional powdered wire drawing. Wet wire drawing is commonly used, in particular, in the production of high-carbon steel cord [6]. Although the drawing speeds already exceed 1000 m/min, even greater speeds are sought after to further improve productivity. However, increasing the drawing speed intensifies heat generation. Approximately 95 % of the mechanical energy involved in the metal forming process is transformed into heat. Another technical challenge is that the excessive temperature rise followed by rapid quenching leads to thermal fatigue, rendering the wire brittle, which eventually leads to wire breaks. This poses new demands on the lubricity, cooling efficiency and thermal stability of lubricants used in the drawing process.

The heat is generated due to friction, and due to material deformation. The heat flow coming from friction is proportional to the drawing speed, and the heat flow coming from material deformation is proportional to the drawing speed squared. To reduce heat intensity, dies with extended reduction zone are sometimes used – by halving the reduction angle, one halves the local shear rates within the wire body, thus reducing the heat coming from the material deformation by a factor of four. Unfortunately, the heat due to friction is doubled at the same time. Furthermore, using a too small reduction angle increases the risk of air entrapment, sporadically causing unlubricated friction events leading to premature wear of the die.

Figure 7. Principle of wire drawing process: the crosssection is reduced by pulling it through a conical die (ϕ is the reduction angle)

Using vegetable-based lubricity components in drawing oil formulations ensures the formation of a uniform and resilient lubricating film, even when a minimum quantity of lubricant is used. In the presence of such a film, the range of elastohydrodynamic lubrication is greatly extended [7,8] and EP additives start to react before unlubricated contact occurs. Due to reduced friction, heat is reduced and quenching gets milder. As a result, higher drawing speeds can be sustained, die lifetime extended and overall process runnability improved. E-ION lubricity additives excel also in difficult drawing operations, such as drawing of Cu, Zn and brass-coated steel wire, without damaging the coating.

5. CONCLUSIONS

Lubricity and oiliness components produced by $Elektrionization^{TM}$ of vegetable oils serve a solid foundation for addressing performance challenges in formulation of metalworking lubricants for operations

such as cutting, drilling, deep drawing, wet wire drawing, rolling, forming, etc. This type of lubricity and fatty oiliness additives has the following benefits:

- enhanced wear protection and extended tool life,
- clean running and excellent surface finish,
- better process runnability and ability to operate at higher speeds,
- reduced lubricant consumption,
- better emulsion stability in the case of soluble oils and
- improved environmental and health safety profile.

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БИЉНА УЉА ДОБИЈЕНА *ELEKTRIONIZED™* ПОСТУПКОМ КАО КОМПОНЕНТЕ ЗА ПОБОЉШАЊЕ МАЗИВОСТИ СРЕДСТАВА ЗА ХЛАЂЕЊЕ И ПОДМАЗИВАЊЕ ПРИ ОБРАДИ МЕТАЛА

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Адитиви за побољшање мазивости, познати и као модификатори трења, константно наилазе на прихватање од стране инжењера за подмазивање. Презентовани рад се фокусира на примену ових адитива у формулацији средстава за хлађење и подмазивање при обради метала, као што су права уља и средстава са водом, објашњавајући како ови адитиви функционишу и који су параметри који контролишу својство мазивости код готових производа. Показано је да за разлику од адитива за велике притиске, који делују када дође до директног додира површина у условима граничног подмазивања, јонизована биљна уља делују тако што одлажу појаву граничног подмазивања.