

## THE AFTERMARKET ADDITIVES USED IN LUBRICATING OILS

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### Abstract

The paper presents literature review concerning the aftermarket additives used in lubricating oils. Classification, principle of operation and scientific research of aftermarket additive operational effectiveness was presented. In majority of cases lubricating oils modified by aftermarket, additives are tested by means of a four-ball extreme pressure tester T-02 or friction machine T-05. Tester T-02 is used to determine lubricating oil parameters like weld load  $P_z$ , maximum non-seizure load  $P_n$ , seizure load  $P_h$ , load wear index  $I_h$  and load limit of wear  $G_{oz}$  according to Polish Norm (PN-76/C-04147). Investigation of the tribological properties (friction force, wear of the matching elements) is executed by means of friction machine T-05.

Until now, scientific research does not result in unequivocal assessment of the aftermarket additives. It come from big variety of aftermarket additives (chemical interaction aftermarket additives, additives that contain molecules of solid lubricants, additives that are able to form conditions for selective transfer lubrication) and their various principles of operation.

Now the chemical interaction aftermarket additives have the widest application. These additives join permanently with lubricating oil, so they do not precipitate on the filters and do not create heat-insulating layers unlike the additives which contain molecules of solid lubricants (for example PTFE). Chemical interaction aftermarket additives improve antiwear (AW) and antiseizure (EP) properties of lube oils, decrease temperature in friction area and consequently minimize wear of the machines metal elements. Their functioning efficiency is usually the highest in hard working conditions (high loads, polluted environment, deteriorating technical condition of friction node elements) and in case of oils worse equipped with AW and EP additives (machine and hydraulic oils). In case of polymers, the influence of aftermarket additives is ambiguous.

**Keywords:** lubricating oils, aftermarket additives, boundary layer, wear

### 1. Introduction

The proper lubrication assurance is one of the most important problems in machines construction and operation. The main reason for productivity loss of machines (85-90%) is wear caused by friction [2]. According to [8] 50% of fuel consumed by transport facilities is lost in their friction nodes.

Applied lubricants (oils and greases) are characterized by still improving properties. Lubricants quality improvement is obtained by additives, which are their integral part. Nevertheless, in extreme hard working conditions of the friction nodes (high pressures, velocities and temperatures, temporary lubricating lack during starting) the machine elements are not secured enough. In connection with the above mentioned the idea to introduce the additional substance – aftermarket additive into lubricating oil systems (with the lubricating oils) was put forward.

Until now, scientific research does not result in unequivocal assessment of aftermarket additives operational effectiveness. It comes from big variety of aftermarket additives added to various lubricating oils, which work in different operating conditions. Generally speaking aftermarket additives are kind of antiwear (AW) and antiseizure (EP) additives used for some special aim for example to improve working conditions of friction node elements by increasing boundary layer stability. In the consequence of sorption and chemisorption new boundary layer

(independent of boundary layer created by AW and EP additives added to lubricating oil by manufacturer) is formed on cooperating elements surfaces. These “double” boundary layers are able to carry bigger load and also friction resistances and wear of these elements decrease. In the result lubricating oil service life increases and device operating cost decreases. There is also positive ecological effect connected with lubricants utilization [4, 7, 25].

The paper presents literature review concerning the aftermarket additives used in lubricating oils – classification, principle of operation and scientific research of aftermarket additives operational effectiveness.

## 2. Classification and principle of operation of the aftermarket additives

Aftermarket additives may be divided into three main groups [9]:

- chemical interaction additives,
- additives which contain molecules of solid lubricants,
- additives which are able to form conditions for selective transfer lubrication in tribosystem.

Chemical interaction additives are lubricating oil soluble long chain compounds with a polar group at the end or compounds based on zinc dithiophosphate which additionally contain phosphorous, sulphur or chlorine. These additives are introduced into machine friction nodes with different kinds of lubricating oils. The chemical interaction additives molecules in increased temperatures react with metallic foundation. Finally, the boundary layer resulting from sorption and chemisorption phenomenon and self-regenerating diffusion layer, which is additional protection of cooperative elements, are obtained. It is necessary to note that the boundary layers on machine elements arise similarly in case of lubricating oils with chemical interaction aftermarket additives as well as lubricating oils with additives introduced by oil manufacturer only. The difference is that the chemical interaction aftermarket additives added to lubricating oil increases active matter concentration, so thicker and faster boundary layer can be formed, which is able to withstand considerable higher dynamic and thermal load of the friction node elements.

The aftermarket additives, which contain molecules of solid lubricants, can be divided as follows:

- substances with lamellar structure for example: graphite, molybdenum disulphide ( $\text{MoS}_2$ ), wolfram, nitrides, sulphates,
- substances with small internal cohesion for example: soaps, solid waxes, plant fats, soft, polymers (polytetrafluoroethylene) and soft metals (copper, tin, lead, silver) usually in powder.

The substances with lamellar structure are characterized by clear determined cleavage planes and slip planes which proceed along separate layers. Two theories – structural and adsorbent try to explain the idea of lubrication with lamellar structure substances. The first one explains lubricating properties by lamellar structure of the lattice which is characterized by easily polarized small positive and big negative ions in lattice points. The atoms laying in flat layer are interconnected by strong covalent bonds whereas between the layers there are weaker electrostatic bonds. According to second theory - adhesion of the substance molecules on the metal surface is the determining factor. Presumably, good lubricating properties are obtained when both of the above-mentioned requirements are performed. The polytetrafluoroethylene (PTFE) is an example of small internal cohesion substance. The PTFE is inserted into lubricating system in the form of sub-microscopic spherical particles. The way of its action depends on particles electrical activity. The particles which have positive charge are connected with metal surface as a result of electrostatic interaction. If the distance between friction node elements is radically reduced the PTFE particles adsorbed on roughness tops will be rolled. The PTFE film formed in that way is 1-2  $\mu\text{m}$  thick and its adhesion to metal surface is so great, that removal is possible only by grinding. The particles, which are electrically neutral, do not form films on metal surfaces. In that case the spherical PTFE particles operate as ball bearings.

PTFE is characterized by the smallest values of friction factors among solid substances (for PTFE/PTFE – 0.04; for steel/PTFE – 0.09-0.14) [18] and complete chemical inertness in relation to lubricants, metals, rubbers etc.. So, the PTFE film formed on the metal surfaces considerably decreases friction resistances and wear in boundary friction conditions. Additionally PTFE film protects against corrosion and different disadvantageous chemical processes. On the other hand that film decreases clearances between friction node elements and makes insulating layers. It is disadvantageous effect because it may cause temperature rise in friction area and extreme seizing. In lubricating oil systems the ball-shaped PTFE particles precipitate on the oil filters. Finally, the filters are fouled and the substance which was expected to perform a special task is eliminated from lubricating oil. These factors resulted in the fact that PTFE is not used in practice.

The soft metals like: copper, tin, lead, silver are different example of substances with small internal cohesion. Aftermarket additives based on soft metals are characterized by all above mentioned PTFE defects. Their operation is also similar to PTFE particles. Additionally the soft metals (especially copper) strongly catalyse the disadvantageous process of lubricating oil oxidation. These factors caused the lack of application of aftermarket additives based on soft metal.

The selective transfer phenomenon consist in spontaneous regeneration of worn surfaces as a result of building in molecules from different places of the friction node. The authors of discovery are Prof. D. Garkunov and Prof. I. Krageskij. It was found that in friction of copper alloys on steel under condition of boundary lubrication, a phenomenon of selective transfer of cooper from the solid solution of copper alloy to steel and its reverse transfer from steel to copper alloy occurs.

Aftermarket additives which are able to form conditions for selective transfer lubrication in friction nodes (for example: glycerine and its alcoholic solution, weak organic acids formed by lubricating oil oxidation process etc.) are characterized by reduction properties. They reduce cupric oxides to pure copper. As a result of friction, which causes micro-plastic deformations of the surface layers and temperature raise, the copper ions are able to diffuse into steel surface free from oxides. The copper layer 1-2  $\mu\text{m}$  thick, formed in this way is strongly bounded with metal surface. The friction coefficient and wear decreases about 2-3 orders of magnitude [3].

### 3. Research results of aftermarket additives operational effectiveness

Until now, scientific research does not result in unequivocal assessment of aftermarket additives operational effectiveness. It comes from big variety of aftermarket additives added to various lubricating oils, which work in different operating conditions.

In majority of cases lubricating oils modified by aftermarket, additives are tested by means of a four-ball extreme pressure tester T-02 or friction machine T-05. Tester T-02 is used to determine lubricating oil parameters like: weld load  $P_z$ , maximum non-seizure load  $P_n$ , seizure load  $P_t$ , load wear index  $I_h$ , load limit of wear  $G_{oz}$ . The methodology of the tests is compatible with the Polish Norm (PN-76/C-04147). Investigation of the tribological properties (friction force, wear of the matching elements) is executed by means of friction machine T-05.

In case of engine oils provided with antiwear (AW) and antiseizure (EP) additives by the manufacturer, chemical interaction aftermarket additives do not improve lubrication oil parameters or improve them very slightly and even sometimes impair some of these parameters. The influence of chemical interaction additive on lubricating properties of Superol CC SAE-30, 10W40 Turbo Diesel and Selektol Special SD 20W/40 engine oils was described in [12, 14, 16]. Among determined lubricating oil parameters, only  $P_z$  and  $G_{oz}$  increased. It testifies that chemical interaction additive advantageously acts in extremely hard working conditions. The rest parameters ( $P_t$ ,  $I_h$ ,  $P_n$ ) stay on the same [12, 14] or even a little lower level [16]. In case of aftermarket, additives based on solid lubricants (copper particles, lead particles and molybdenum disulphide) added to CE/SF SAE 15W/40 engine oil, all determined lubricating parameters increased [17]. But aftermarket additive based on soft metals included copper and lead particles

5 to 15  $\mu\text{m}$  in diameter. It makes impossible application of these additives in engine oils because of copper and lead particles are separated in lubricating oil filters.

Ceramic particles with diameter less than 2  $\mu\text{m}$  added to lubricating oils do not clog filters and cover matching elements improving sliding properties of the friction node. Comparative investigations of Castrol Magnatec Diesel 10W-40 engine oil modified and not modified by aftermarket additive based on ceramic particles showed that micro ceramic had positive influence on lubricating properties parameters. The balls average wear (determined by average scar diameter) reduced and load limit of wear increased [19]. It is necessary to note that for the lowest load applied the scar diameters were the same. It means that positive influence of aftermarket additive reveals in hard working conditions of the friction nodes.

Interesting results of applied research were presented in work [12]. Superol CC SAE-30 engine oil used in Jelcz SM-200 buses was modified by chemical interaction aftermarket additive. Compression pressure in engine cylinders, starting current, smokiness of combustion gas and fuel consumption were tested before and after 2000 kilometres of run. Compression pressures in engine cylinders raised, starting current and smokiness of combustion gas reduced. It is necessary to note that simultaneously fuel consumption raised a little (about 2%). Growth of fuel consumption is probably caused by viscosity growth of lubricating oil and aftermarket additive mixture what in fluid lubrication conditions results in raising of friction resistances.

In marine engines, the aftermarket additives are not used up to now. Besides filtering, lubricating oils used in marine engines are purified. In connection with it the question arises if the aftermarket additives (which have higher density than oils and water) are able to join permanently with lubricating oil in order not to separate in the purifying process and what influence they have on lubricating oil ability to separate the water. The lubricating oil with chemical interaction aftermarket additive and water purifying research which aim was to answer the above questions were presented in works [23, 24]. Aftermarket additive was not separated from lubricating oil during purifying. Additionally in case of soot contamination, the tested additive improved the oil ability to remove water.

Application of aftermarket additives in toothed gears working in especially hard conditions for example in devices used in oil and gas exploration and in mining (high loads, pollution, aggressive environment) would be well-founded. Lubricating properties of Spirax HD 90 gear oil modified by chemical interaction and based on soft metals aftermarket additives research results were presented in work [10]. As a result slight improvement of lubricating properties was obtained (parameters  $I_h$ ,  $P_t$ ,  $G_{oz}$  increased but  $P_z$  and  $P_n$  remained on the same level). Between two tested preparations, better effects were obtained for chemical interaction aftermarket additive. It is necessary to note very high growth of  $G_{oz}$  parameter (about 428%) with chemical interaction aftermarket additive application. It testified for ability to stand high pressures.

Machine oils (AN-46, AN-68) modifying considerably improves all lubricating parameters [11, 13]. However, the question arises if the oils with so high lubricating properties parameters should be used for lubrication machines elements, which are not high, loaded (guides, spindles etc.).

Generally, aftermarket additives decrease movement resistances and wear of the matching elements, in boundary friction conditions, if these elements are made of metals (cast iron, steel, bronze) [6, 13, 15, 20]. Probably it results from changes on matching elements surfaces - surface roughness decreases and real contact surface increases. However, in case of polymers the influence of aftermarket additives is ambiguous. In work [1] two aftermarket additives were tested: chemical interaction additive and additive based on synthetic ceramic particles. The friction node elements were made of politetrafluoroethylene (PTFE) or its composites and steel. In case of not modified PTFE or its composites with stainless steel and aluminium, powder the wear of the polymers increases when aftermarket additive is added to lubricating oil. Whereas in case of PTFE composite with tin bronze or glass fibre the wear of the polymers decreases. Therefore, application of aftermarket additives requires a lot of care when friction node elements are made of PTFE or its composites.

#### 4. Conclusions

1. There is not unequivocal assessment of the aftermarket additives. Different opinions about aftermarket additives functioning can be found in the professional literature – from harmfulness or weak effectiveness to good efficiency and big technical, economical and ecological meaning. Such different opinions come from big variety of aftermarket additives and their various principle of operation.
2. Now the chemical interaction aftermarket additives have the widest application. These preparations join permanently with lubricating oil, so they do not precipitate on filters and do not create heat-insulating layers.
3. Aftermarket additives improve antiwear (AW) and antiseizure (EP) properties of lube oils, decrease temperature in friction area and consequently minimize wear of the machines metal elements. The functioning efficiency of the aftermarket additives is usually the highest in hard working conditions (high loads, polluted environment, deteriorating technical condition of friction node elements) and in case of oils worse equipped with AW and EP additives (machine and hydraulic oils). In case of polymers, the influence of aftermarket additives is ambiguous.
4. Chemical interaction aftermarket additives added to engine oils results in increase of compression pressures in engine cylinders, decrease of starting current and combustion gas smokiness and a little increase (about 2%) of fuel consumption caused probably by viscosity growth of lubricating oil and aftermarket additive mixture what in fluid friction conditions results in raising of friction resistances.
5. Lubricating and tribological properties investigations made on friction machines do not show fully working conditions existing in combustion engines or toothed gears. So as to determine the influence of aftermarket additives on matching elements wear, investigation on real object should be done.

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