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Lubricity additives for motor fuels

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The paper describes the origin of insufficient lubricity properties of motor fuels, the essence of the problem and laboratory test methods applied to determine fuel lubricity. Ways applied by fuel industry to enhance lubricity are presented. There was also carried out a patent analysis concerning lubricity additives and fuel compositions. The anti-wear behavior of lubricity enhancers, their types and possible undesirable effects were described.

Keywords: lubricity, fuels, lubricity enhancers, boundary lubrication

Introduction

Since the end of '70s there was observed increased concern about natural environment and also in this period there appeared laws and regulations concerning environmental issues. Some of them forced to reduce pollution of automotive origin because cars are one of the largest sources of air pollutants. The majority of legislative initiatives concerning tailpipe emission was introduced in the '80s. Among others, they concerned reduction of lead content in gasoline as well as sulfur and aromatics in diesel fuel. At that time appeared also such terms as environmentally-friendly fuels, clean burning fuels and reformulated fuels. Automotive fuels are still mostly fossil derived and are complex mixtures containing hundreds of chemical components, mainly hydrocarbons (constituting the bulk of the fuel). They have to satisfy various engine types, different operating conditions and fuel system technologies and to meet efficiency and environmental requirements. Sulfur compounds are naturally occurring constituents of crude oil. They are removed from it in refinery upgrading processes for their odour, acidic nature and the fact that they are known to be strong catalytic poisons. However, severe hydrotreating necessary to remove sulfur produces fuels having poor lubricating ability what, in turns, may lead to failure of the engine injection equipment. Additionally, deterioration of lubricating ability results also from increased injection pressures (ca. 2000-2500 bar) applied in modern engines. To restore lubricity, the refinery industry uses various lubricity additives (called also as: friction modifiers, lubricity enhancers or lubricity improvers).

1. Lubricity of motor fuels and its evaluation

Fuel pumps and injection equipment of internal combustion engines are fuel lubricated. No external lubricant is used. Because of very fine tolerances, the moving components operate under boundary lubrication conditions, i.e. there is a very thin film adhering to friction surfaces that reduces friction and prevents wear and failure. Boundary films are formed by physical bonding (van der Waals forces), chemisorption and chemical reactions. Under boundary lubrication conditions the viscosity of lubricant is not a friction controlling parameter. To describe the anti-wear behavior of lubricant it is used a term "lubricity". This term appeared at the end of the 19th century. At that time more popular terms were "oiliness" and "body" introduced by A. Kingsbury [1] to describe differences in lubrication behavior for fluids with the same viscosity and it has been used with reference to mineral oils. "At low speeds, especially under heavy loads, and in all cases where a complete oil film cannot form be-

tween the friction surfaces, the viscosity and the oiliness (lubricity, unctuousity) of the lubricant are of great importance" [2].

With the development of science and technology, the term "lubricity" has been modified but there is not established an unequivocal definition of lubricity and its measure. According to R. Marczak [3], lubricity consists of phenomena and processes occurring in the friction zone which depend on the kind of lubricant, solids and atmosphere. Lubricity is not a physical property of a fuel. It is a conventional concept indicating ability to generate boundary layers that protect against excessive wear. As opposed to viscosity, that is an individual property of fuel, lubricity is a complex property – a property of the whole tribological system because it depends on conjunction of phenomena occurring in the friction zone. Lubrication is insufficient when there is a lack of a resistant enough boundary layer able to separate completely surfaces moving against each other.

Problems associated with inadequate fuel lubricity occurred for the first time in the 60s and were related to injection equipment failures in aircraft engines [4]. Later, during the Vietnam War, users of turbo aircraft engines experienced similar problems. At that time started efforts aimed to develop tests for aircraft fuel lubricity evaluation. First attempts were performed using Dennison tribotester [5] but the obtained results showed poor correlation with field trial results. Many wear tests designed to evaluate lubricants (e.g. Almen, Timken, SAE, four-ball) were applied in search of fuel lubricity test [6]. However, the obtained results did not provide satisfactory results. In 1971 R.T. Aird [4] developed Lucas Dwell Test – the first test dedicated for fuel lubricity evaluation. The method gained some interest in the 1970s, mainly in Great Britain. In the year 1985, J.W. Hadley [7] built the Thornton Aviation Fuel Lubricity Evaluator (TAFLE) by modification of the Amsler machine. TAFLE apparatus has not been widely used because of an expensive and complex procedure but it was successfully applied in individual cases up to 1990s to estimate aviation and diesel fuel lubricity properties [8]. There exists only a prototype of this apparatus. In the late 1960s, the British Ministry of Defense formed a working group to develop a standard method of aviation fuel lubricity evaluation. As a result, the ball-on-cylinder apparatus designed by M. Furey in 1961 [9] was adapted to create the BOCLE test (Ball-on-Cylinder Lubricity Evaluator) [10]. In 1990, after several modifications, the test was accepted as an ASTM standard for measurement of jet fuel lubricity [11].

Diesel fuel as a liquid hydrocarbon-based fuel shows rather poor lubricity properties. However, natural high-sulfur diesel has good lubricity because of the presence of heavier hydrocarbons and trace polar species originated from crude oil. Diesel fuel lubricity problems occurred for the first time in late 80s. The most stringent regulations regarding the sulfur content were introduced first (1988) in California and then in Sweden and Finland. The amount of sulfur in diesel fuels was reduced from 2000-5000 ppm even up to 10 ppm ((Swedish Class I). High reduction level of sulfur compounds and aromatic hydrocarbons (two- and three-ring mainly) in diesel fuels during hydrotreating was accompanied by reduction of nitrogen- and oxygen-containing polar constituents that were removed as a by-product. Low lubricity diesel fuel causes failure and premature wear of injection equipment – rotary and distributor-type injection pumps which are completely fuel lubricated. To maintain its

good lubrication quality, the inclusion of lubricity enhancing additives is needed. Attempts to monitor effectiveness of these additives forced researchers to develop appropriate procedures.

As a result of the US Army sponsored study, P.I. Lacey [12] adapted the BOCLE test procedure in order to reproduce the predominant wear mechanisms occurred in fuel injection equipment. The modifications related to the friction couple, test conditions as well as evaluation criteria. The modified procedure is commonly referred as SLBOCLE (Scuffing Load BOCLE) [13]. SLBOCLE is the most popular in the United States where it was accepted as a standard test method for evaluating lubricity of diesel fuels. Another modification of the BOCLE test was done by J.W. Hadley [11] and was called BOCLE (Lubrizol/Hadley) but this procedure is used rarely.

HFRR (High Frequency Reciprocating Rig) – procedure designed to assess diesel fuel lubricity – was developed in 1986 by H.A. Spikes and D. Wei [14]. The procedure was widely practiced after modifications done by C. Bovington [15]. The test consists in high frequency reciprocating motion of a loaded steel ball over a static steel plate immersed in the investigated fuel at the specified test temperature. A measure of diesel fuel lubricity is the value of wear scar diameter corrected to the standardized water vapour pressure of 1.4 kPa and is denoted as WS1,4 (Wear Scar). Generally, the test is performed at 60°C. Lower test result values reflect better lubricity. Another attempt to monitor diesel fuel lubricity was modification (by Falex) of the well-known four-ball test [16]. The modified version is called BOTD (Ball-on-Three Discs). Attempts to investigate on diesel fuel lubricity were also done by D. Cooper [17] who developed a test procedure based on the Plint TE-77 test rig. Among the existing methods for diesel fuel estimation, the HFRR test is the most popular and the most frequently used.

2. Fuel lubricity additives

The worldwide initiatives concerning fuel quality improvement led to limit the sulfur content in transportation fuels up to 10 ppm in Europe (EN 590) and 15 ppm in the United States (ASTM D975). Such deeply desulfurized diesel is called ultra-low sulfur diesel (ULSD). In Europe, ULSD specification started in 2009 (for on-road vehicles) and in 2011 (for non-road vehicles). ULSD fuel requirements in the USA became effective in 2006. At the refinery, ultra-low sulfur diesel shows very poor lubricity (typical HFRR wear scar is over 600 μm [18]). Such fuel is considered as “dry”. To provide good fuel properties, lubricity requirements were introduced into diesel specifications. ASTM accepted HFRR and SL-BOCLE tests and ISO accepted the HFRR method. The maximum HFRR wear scar acceptable by EN 590:2013+A1:2017 is 460 μm and by ASTM D975-18 – 520 μm, although, the Worldwide Fuel Charter recommends 400 μm for markets with advanced requirements for emission control [19].

Problems associated with inadequate fuel lubricity may be solved through:

- proper feedstock selection and fuel processing technology in order to maximize the content of constituents having good lubricity properties,
- blending fuel with components having good lubricating characteristics,
- application of lubricity additives.

In practice, the third solution is most often applied by fuel industry. This is also the most cost-effective way. Fuel additives are chemical substances that are added to fuels in order to enhance desirable or to suppress undesirable properties. The global fuel petroleum additive market is growing rapidly to satisfy the demands of more and more stringent quality requirements. From 2007 to

2012 the demand for fuel lubricity additives grew at an above average rate of 3.5% a year [20]. Lubricity additives are on the market since the early 90's. The approximate dates of introduction of major fuel additive types are presented in Fig. 1.

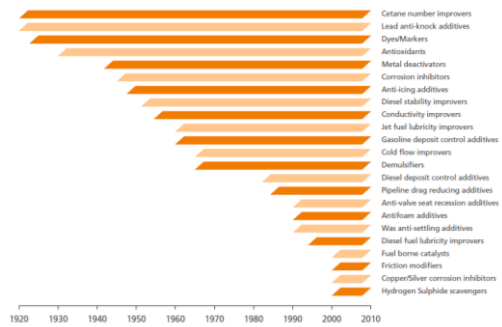


Fig. 1. The approximate dates of introduction of major fuel additive types [21]

Chemical compounds used as fuel lubricity additives have to fulfill the following criteria:

- contain a polar functional group which increases the rate of absorption on metal surfaces,
- contain an olefin chain to provide solubility in the fuel composition,
- ash-forming components are not allowed in their composition,
- do not contain elements acting as catalyst poisons, such as sulfur, phosphorus or boron,
- do not show corrosive action towards the fuelling system,
- do not show negative impact on exhaust emission.

Lubricity additives comprise a range of surface-active chemicals. Generally, they are long chained (usually C12-18) hydrocarbon molecules with small polar functional groups, i.e. with hydrocarbon “tails” and polar “heads”. To be effective, the additive molecule should contain a polarity-imparting heteroatom, preferably oxygen. Most commercial lubricity improvers are: carboxylic acids and their salts, amides, alcohols, ethers and esters. Generally, they are classified based on their chemistry as neutral (amides and esters) or acidic (mono-acidic or dimer acids). Additives, thanks to their affinity, provide bonding to the metal surface and form a protective layer on it (Fig. 2). Polar heads attract to the metal and long hydrocarbon chains are normal to the surface creating a fluid barrier between surfaces. Carboxyl and hydroxyl groups form hydrogen bonds with the metal surface. Film forming ability of esters provide carbonyl groups. Polar groups may be aligned according to their ability to increase lubricity as follows: – COOH (carboxylic acids) > CHO (aldehydes) > OH (alcohols) > COOCH₃ (methyl esters) > C=O (ketones) > C–O–C (ethers). [22].

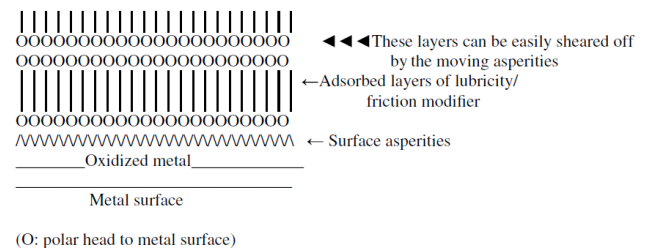


Fig. 2. Adsorption of a lubricity additive on the metal surface [20]

Better lubricating properties have additives with stronger polarity, higher unsaturation level and those containing more hydroxyl groups in the molecule. The best lubricity enhancer is the carboxyl group [23].

Dimer acids were one of the first additives applied to enhance lubricity and were mostly used by aviation industry. However, low sulfur diesel fuel treated with them caused serious problems resulting in filter blockage and pump stopping [24]. There was stated the presence of insoluble carboxylate salts coming from acid-base reactions on the cam plates and shafts. Thus, to avoid such problems dimer acids were subsequently removed from the diesel market. World leading companies producing fuel additives are, among others: Ethyl Petroleum Additives, BASF, Afton, Lubrizol Corporation, Chevron, International Lubricants, Exxon-Chemical, Shell Additives, Adibis, E.I. duPont de Nemours and Company, Nalco Chemical Company, Mobil Chemical Company, Petrolite Corporation, Octel-Starreon.

The carried out patent analysis (Table 1) concerning fuel lubricity additives revealed that, generally, fuel compositions and not individual additives, constitute the majority of patent applications.

Tab. 1. Patent applications concerning fuel lubricity enhancement

Patent number	Applica-tiondate	Title of patent application
US 3 273 981	20.09.1966	Anti-wear oil additives.
US 5 490 864	13.02.1996	Anti-wear lubricity additive for low-sulfur content diesel fuels.
EP 0 605 857	13.11.1996	Mineralische schwefelarme Dieselkraftstoffe.
WO 94/17160	22.01.1997	Fuel composition.
JP 09272880	21.10.1997	Fuel oil composition.
PL 174112	30.06.1998	Miejski olej napędowy.
JP 10176175	30.06.1998	Additive composition for fuel oil and fuel oil composition.
US 5 833 722	10.11.1998	Fuel oil compositions with improved lubricity properties.
JP 11001692	06.01.1999	Fuel oil composition.
WO 99/00467	07.01.1999	Fatty acid amide lubricity aids and related methods for improvement of lubricity of fuels.
US 5 858 028	12.01.1999	Fuel oil composition.
JP 11071586	16.03.1999	Fuel oil composition for diesel engine.
US 6 051 039	18.04.2000	Diesel fuel compositions.
EP 1 013 746	28.06.2000	Fuels with enhanced lubricity.
PL 179231	31.08.2000	Low-sulfur diesel fuel.
PL 180044	29.12.2000	Multifunctional diesel additive.
JP 2001049284	20.02.2001	Fuel oil lubricity improver and fuel oil composition.
EP 1 081 210	07.03.2001	Fuels with enhanced lubricity.
GB 2 354 254	21.03.2001	Fuel composition with improved lubricity performance.
WO 01/36568	25.05.2001	Lubricity improver and a fuel and lubricant composition containing said agent.
US 6 239 298	29.05.2001	Fuel lubricity additives.
GB 2 357 296	20.06.2001	Low sulphur fuel composition with enhanced lubricity.
WO 01/51592	19.07.2001	Gasoline composition.
US 2006/0288638 A1	28.12.2006	Lubricity additive for fuel.
US 2007/0193110	23.08.2007	Fuel lubricity additives
US 2008/0098642	01.05.2008	Lubricity improving additive composition for low sulfur diesel fuel.
US 2009/0056203 A1	05.03.2009	Branched carboxylic acids as fuel lubricity additives.
US 2010/0000484 A1	07.01.2010	Liquid fuel compositions.
US 8,518,128 B2	27.08.2013	Fuel additive composition improve fuel lubricity.
PCT/FR2016/052168	02.09.2016	Lubricity additive for fuel with a low sulfur content.
US 9 476 005 B1	25.10.2016	High-performance diesel fuel lubricity additive.
US 9,745,531 B2	29.08.2017	Fuel lubricity additive.
US 2018/0187110 A1	05.07.2018	Lubricity additive for fuel with a low sulphur content.
US 9,745,531 B2	29.08.2017	Fuel lubricity additive.
US 2018/0127675	10.05.2018	Dialkylaminoalkanol friction modifiers for fuels and lubricants.

Choosing a fuel lubricity additive one should take into consideration mostly: effectiveness, cost and no-harm performance. Although one chemical improves some fuel characteristic, it may deteriorate the other ones or influence negatively engine operation. Thus, addition of an additive in the fuel should be carefully analysed [25]. Generally, lubricity enhancers do not influence negatively the engine exhaust emission. However, some diesel lubricity additives were reported to react with crankcase lubricating oil. In result, sticky

carbonaceous deposits on plunger surfaces were detected [26]. Another negative effect may result from sodium contamination of diesel fuel. sodium hydroxide and a fuel soluble salt – sodium 2-ethylhexanote interact with mono-acid lubricity additives producing filter blocking and injector sticking [27].

To be effective in wear reduction, lubricity additives have to be mixed with the fuel at proper concentration. Fuel lubricity additive treat levels are generally low, in most cases from 20 up to 200 ppm. At the level over 500 ppm, the additive effectiveness usually decreases. Fig. 3. presents the HFRR scar diameter reduction with the "treat rate" of an additive [28]. At low concentrations (region I), the surface is incompletely covered by adsorbed additive particles which do not support anti-wear action. Increased additive concentration (in the region II) results in wear lowering due to formation of a coherent but still incomplete film. At certain additive concentration (transition point from the region II to the region III) the boundary layer is complete and protects the surface against wear. Further increase in concentration does not reduce the wear scar diameter.

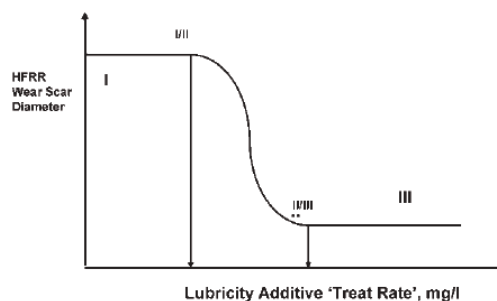


Fig. 3. Effect of lubricity additive concentration on wear reduction [28]

Another way to restore diesel fuel lubricity is blending it with high lubricity fuel. The most common practice is blending low sulfur diesel with commercial biodiesel (vegetable oil or animal fat based diesel fuel, consisting of long-chain mono-alkyl esters), usually at a level of 1–2%. [29,30]. Biodiesel possess very good lubricating properties because its main constituents are neat fatty esters. Additionally, biodiesel contains also minor constituents (usually considered undesirable) formed during the transesterification reaction, such as neat free fatty acids, monoacylglycerols and glycerol. These constituents possess better lubricity than neat esters because of their free OH groups [31]. The required biodiesel level exceeds the typical additive level but this does not create problems because biodiesel properties are compatible with petrodiesel. However, some problems may arise if the blends would take up water. Since the saturation level of moisture in biodiesel is 15–25 times higher than that of petrodiesel (in the range of 4–35°C) and diesel fuel lubricity decreases linearly with the moisture content, this issue should be avoided [32].

Lubricity problems concern also gasoline [33,34] and became more urgent with the development of direct injection because high injection pressures and low lubricity may lead to the failure of injection equipment.

Summary

Severe hydrotreatment technologies are applied by the petroleum industry to remove sulfur compounds from automotive fuel base stock. However, desulfurization removes also heavier hydrocarbons and trace polar species originated from crude oil what results in a deterioration of lubricity properties. One of the most commonly applied method to meet fuel specification and restore fuel lubricity is application of lubricity additives i.e. surface-active compounds (long

chained hydrocarbon molecules with small polar functional groups) added to the fuel base stock during final blending. Additives provide sufficient boundary layer lubrication. They may be acidic or neutral. Mostly applied are mono-carboxylic acids and esters. One of the most important feature of lubricity additives is their no-harm performance. Interaction with other fuel components should be carefully analysed to prevent adverse side effects.

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Dodatki smarnościowe do paliw silnikowych

W artykule opisano genezę problemu smarności paliw silnikowych, jego istotę oraz metody badania właściwości smarnych. Przedstawiono sposoby podwyższania smarności paliw stosowane w przemyśle petrochemicznym. Dokonano również analizy literatury patentowej w tym zakresie. Omówiono mechanizm działania dodatków smarnościowych, ich rodzaje oraz możliwe działania niepożądane.

Słowa kluczowe: smarność, paliwa, dodatki smarnościowe, tarcie graniczne

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