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Alternative eco-friendly lubes for clean two-stroke engines

A. Igartua [a,*], R. Nevshupa [a], X. Fernandez [a], M. Conte [a], R. Zabala [b], J. Bernaola [b], P. Zabala [b], R. Luther [c], J. Rausch [c]

[a] Fundación Tekniker, Avda. Otaola 20, Eibar 20600, Spain
[b] Abamotor Energía, SL, B. Astola, 6, Abadiano 48220, Spain
[c] Fuchs Europe GmbH, Friesenheimer Str. 15, Mannheim D-68169, Germany

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High performance lubricant for clean two-stroke engines operating with ethanol-containing fuels was developed by the selection of the optimal synthetic esters base oil followed by an improvement of the additives composition. The developed lubricant has very good wear resistance, ashless and low carbon soot deposit formation. The lubricant has low toxicity for aqueous organisms (algae and Daphnia Magna) and high biodegradability. Good wear resistance and low friction were achieved because of formation of a protective transparent friction lacquer on the contact surface due to tribochemical reactions.

1. Introduction

Since its invention in the last quarter of the nineteenth century and during all the twentieth century, two-stroke engines penetrated in many industrial, automotive and handheld applications where engines with high specific power, simple design, light overall weight and low cost were required. Presently, two-stroke engines are commonly used in motorcycles, scooters, chainsaws, outboard applications, agricultural machinery, lawnmowers, etc.

Usually, the moving parts of a two-stroke motor are lubricated either by using a mixture of oil with petrol or by pumping oil from a separate tank. Both designs use total-loss lubrication method, with the oil being burnt in the combustion chamber. Therefore, the lubricating oil must meet specific requirements: it must have an optimal balance of light and heavy oil components to lubricate at high temperature; it should not produce deposits (carbon soot and other) on moving parts, and it should be ashless. In addition, the oil should provide good protection of moving parts at high speed under deceleration of the engine with the throttle closed, when the engine usually suffers from oil-starvation. Finally, in the view of this paper, the two-stroke oil should be compatible with alternative fuels, containing varying quantities of ethanol. In one sentence: those oils have to be multi-talented.

Also, two-stroke engines produce more contaminations than four-stroke engines, due to oil burning in the combustion chamber. Therefore, it is very important to reduce these contaminations to meet ecological requirements—this is known as "low smoke behaviour".

Another challenging issue of the European technological strategy resides in complete substitution of fossil-based fuels and lubricating oils with renewable eco-friendly and high performance materials. Esters were identified as alternative base oils because of their normally high biodegradability and low toxicity, combined with excellent lubricity and low evaporation; additional advantage is their potential derivation from natural, renewable resources [1]. Synthetic esters are characterized by their polar structure, high wear resistance, good viscosity-temperature behaviour, miscibility with non-fossil fuels. Ester-based oils can be blended with various components like antifoam agents, oxidation inhibitors, pour-point depressant, antirust agents, detergents, antiwear agents, friction reducers, viscosity index improvers, etc., to create environmentally compatible prototype engine oils and to meet the changing environmental requirements in low sulphur fuels and other alternative fuels and their application to engine oils. Low content of metal additives and clean-burn characteristics result in less engine fouling with much reduced ring stick and lower levels of dirt built-up on ring grooves, skirts and undercrowns. Due to the presence of polar ester groups in the molecule, giving increased adhesion to metal surface, esters have much better lubricity, than hydrocarbons. Furthermore, the performance of ester-based lubricating oils can be improved by selecting suitable additives. Since ester oils have much better lubricity, the additive content, especially anti-wear, can be reduced. So, this work is aimed at the comparative

* Corresponding author.
E-mail address: aigartua@tekniker.es (A. Igartua).

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characterization of various fully formulated prototype engine oils based on synthetic esters and mineral reference oil for two-stroke engines.

2. Materials and methods

Three different synthetic ester oils have been selected to formulate three prototype engine oils with the same additive composition. These oils are different mixtures of fully saturated polyol-ester and mono-ester types and are designated as SEMO 4, SEMO 5 and SEMO 10. The additives composition of these three oils is the same; however, they differ in the base oil composition. All of these two-stroke engine oils are ash-free without Zn, Ca, Mg or other metal-containing additives and without phosphorus too. After comparative characterization of these prototype oils and selection the oil with the best tribological performance (SEMO 10), a new improved formulation miscible with bioethanol was developed and designated as SEMO 36. This last oil contains phosphorus but it is ash-free. In addition, conventional mineral oil for two-stroke engines was used as reference oil. This reference oil has different additives composition as compared with SEMO oils and is not ash-free.

Oil viscosity was characterized according to ASTM D-445-09 standard procedure [2], and viscosity index was determined using ASTM D-2270-04 [3].

Unleaded petrol (E228) and bioethanol E85 (mixture of 85% of ethanol with 15% of petrol) were used to test miscibility of the lubricating oils with these fuels. For this purpose two different lubricant/fuel ratios were used. Method A was used to test the general fuel compatibility whereas method B represents application like conditions. Method A: mixture of 90% lubricant in the fuel; Method B: mixture of 2% lubricant in the fuel.

Deposit forming tendency of the oils was characterized by the Coker test at 250 °C during 12 h. In this test the oil is dropping on a hot metal plate (250 °C), which is mounted at a fixed angle to allow the oil to flow down the panel slowly. At the lower end of the plate the oil is collected in a glass vessel to be recirculated to the plate again. After a fixed period of time (12 h) the test is finished, the plate is washed and the deposit formation is rated (from 1 to 10) by weighting and by visual observation by an expert. A rating of 10 represents a clean surface without any deposit.

Biodegradability and toxicity of the lubricating oils were examined according to the recommendations of the Organization for Economic Co-operation and Development (OECD). Biodegradability of lubricating oils was tested using OECD 301F Manometric Respirometry Method [4,5], consisting of measurement of oxygen uptake by a stirred solution of the test substance in a mineral medium, inoculated with micro-organisms. Measurements were performed automatically over 28 days using an enclosed respirometer. Biodegradation is determined as the percentage of oxygen uptake in respect to the theoretical value.

Toxicity of the lubricating oils was studied using “Alga, Growth Inhibition Test” OECD 201 [6] and “Daphnia Magna” 24 h Acute Immobilisation Test OECD 202 [7]. In the “Alga, Growth Inhibition Test”, selected green algae were exposed to various concentrations of the test oils over several generations under defined conditions. The inhibition of growth in relation to a control culture was determined over a fixed period. In the Daphnia Magna method, the effect of oil contained in the water on the microcrustacea Daphnia Magna was determined over an established period of time under defined conditions.

Tribological evaluation of lubricating oils was done using ball-on-disk configuration with reciprocating motion according to the standard procedure DIN 51834-2 [8]. Ball and disk were made of 100Cr6 steel. The ball, 10 mm in diameter, performed reciprocating motion with a stroke of 1 mm and a friction frequency 50 Hz. Normal load was 50 N during short run-in period (45 s) and 300 N during the test (60 min). The ball and the disk were immersed in the lubricating oil, which temperature during the test was constant and 50 °C. Friction force was measured as function of time. Friction coefficient was calculated as the ratio of the tangential force to the normal force. After test completion, diameter of the wear scar on the ball was measured using optical microscope, and, from this data, volume wear of the ball was calculated for each lubricating oil tested.

Tribological simulation was performed using cast iron phosphated piston ring and cast iron cylinder liner using reciprocating motion configuration (Fig. 1). The samples for the tests were cut from real engine parts (Minsel M165 two-stroke engine manufactured by Abamotor Energía, SL) keeping original curved surfaces and surface finishing. The conformal contact between the piston ring segment and the cylinder counterface was reproduced by placing a piston ring segment on a suitable frame, A, and fixing it by means of a clamp, B. Normal load was applied on the frame pushing the ring segment against the cylinder liner sample fixed on the base, C, where a lubricating oil bath was provided.

The piston ring segments performed a reciprocating motion with a stroke of 1 mm and a friction frequency 40 Hz. Normal load was 50 N during short run-in period (45 s) and 300 N during the test (90 min). During the test, the piston ring segment and the cylinder liner sample were immersed in the oil, which temperature was constant at 200 °C.

The mass change of the piston ring segments and cylinder liner sample was determined from weighting the components before and after friction tests. Since the mass change can be due to two competitive processes: (i) wear out and (ii) deposit formation from the oil at elevated temperature, estimation of wear out by weighting can give erroneous results. Indeed, after the tests the surface colour became yellowish and remained after solvent cleaning indicating some sparingly soluble deposits formed on the surface due to some chemical reaction. Therefore, in addition to the determination of the mass change, worn volume was calculated from surface geometry. Surface morphology of the friction zone was studied using white light confocal microscopy at three different zones along the wear track on the cylinder liner sample. The acquired 3D surface images were 0.5 mm wide in the direction of friction and each image contained 138 cross-section profiles of the wear track yielding totally 414 profiles for each

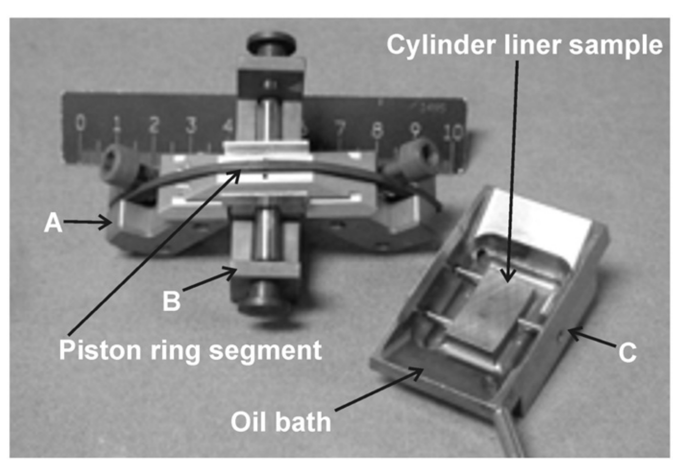

Fig. 1. Experimental set-up for piston ring/cylinder liner simulation. A—frame for fixing the piston ring segment, B—fixing clamp, C—base with oil bath for fixing cylinder liner sample.