



Article Effect of an Aftermarket Additive in Powertrain Wear and Fuel Consumption of Small-Capacity Motorcycles: A Lab and Field Study

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Abstract: Metal conditioners (MC) are friction, wear, and heat-reducing agents between metal components in motion and are mainly used in engines and transmission boxes as aftermarket additives. Laboratory and field tests were conducted to assess the performance of a commercial MC. Laboratory tribotests revealed the MC's potential to reduce wear and friction in lubricated steel contacts. Field studies were performed on two new motorcycles (160 cc) under urban driving conditions for 15,000 km. The physico-chemical properties of the used oils were similar and within the acceptable limits provided in the literature. The FTIR results showed that specific components in the MC formulation do not allow for a direct comparison between oils and their mixtures with MC. Regarding engine wear, MC provided overall aluminum and iron metal parts protection, mainly in the first 7000 km of engine break-in, but a higher wear of copper-containing parts, although at levels below the warning limits. Accurate measurements of engine components demonstrated there were changes of less than 0.05% in the cylinder, piston, and transmission system pieces, except for gear #5. The lubrication of the crown, pinion, transmission chain and gear #5 with the MC significantly increased their wear resistance. The motorcycle driven with MC maintained higher average fuel economy improvements (+1 km/L), representing a 2.5% gain compared to the other motorcycle. Although only two motorcycles were tested, the laboratory and field results suggested that mixing MC with the fully formulated oil (10W-30) reduces wear and friction during the break-in period.

Keywords: powertrain; motorcycles; metal conditioner; aftermarket additives; engine break-in

1. Introduction

Aftermarket additives, added by consumers to lubricant oil, promise to improve the efficiency of internal combustion engines by providing fuel economy, power increase, corrosion and wear protection of moving parts [1]. Among these are metal conditioners (MCs), firmly established on the Brazilian and worldwide market as friction, wear, and heat reducers between the metal pieces in motion [2–4]. In addition, they are proposed to reduce polluting emissions and fuel consumption, while increasing the life of motors and transmission systems [5–8].

In Brazil, metal conditioners currently have no product registration at ANP (*Agência Nacional do Petróleo, gás natural e biocombustíveis*—*Brasília, Brazil*) because they are not registered as additives nor as lubricating oils. Besides (and because of) that, MCs mixed with fully formulated oils have never been tested and approved by oil and large vehicle manufacturers. As a consequence, they have a small market share compared to lubricating oils, which translates into low systematic research on these products. The consequent lack of knowledge about these products has been misapplied by both the companies selling the aftermarket additives, advertising exaggerated performance, and the oil and vehicle manufacturers who are against using them, claiming they cause undesired outcomes when



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). added to fully formulated oils, such as a chemical imbalance of the lubricant, which affects overall oil quality. Reality shows that although their market share is low in comparison to lubricants, it is significant and rises year after year [5,6]. Additionally, in certain specialized applications or industries, these additives may have a place in the improvement of lubrication [2–4], although some customers report component failure after using the product. Therefore, there is a need to regulate and understand such products.

Additives

It is well known that increasing the percentage of a certain additive may improve one property of an oil while at the same time degrading another [9]. For instance, if a high concentration of an anti-wear agent is added to the oil, the corrosion inhibitor may become less effective. The result may be an increase in corrosion-related problems. Furthermore, several additives with excellent extreme pressure (EP) performance, that present significant wear reduction under boundary lubrication, high loads, and sliding speeds, are not usually present in engine oils [10]. These EP additives react with metal (iron) surfaces to form a sacrificial surface film that prevents the welding and seizure of opposing asperities caused by metal-to-metal contact (adhesive wear). However, they can be corrosive toward yellow metals (copper-based metals) [10]. Some examples are sulfur, phosphorus, and chlorine-based EP additives, which are avoided due to corrosion concerns [3,10]. The key is to determine if these additives will bring more benefits by reducing adhesive wear or harm by increasing corrosion [1,3,11–13]. In short, the use of aftermarket additives certainly brings possibilities to improve oil performance but might also cause a chemical imbalance in the lubricant, degrading its overall performance [12].

Most of the publications on MC are from informal sources, since reliable and scientific references are scarce. Here, one should emphasize the work from Alves, D. (2014) [14], Nunes, E. (2014) [15], Santos de Oliveira, F. (2015) [16], and Coppini et al. (2017) [17] that demonstrates that the prior conditioning of cutting tools (enlargement, threading, and drilling) with metal conditioner leads to improved performance, cost reduction, and higher tool life, compared to unconditioned tools. Surprisingly, to the best of the authors' knowledge, there was no peer-reviewed reference about MC performance in powertrains, even though that is its primary application. Contrastingly, there are thousands of papers evaluating the performance of base or fully formulated oils with the addition of additives or nanoparticles using standardized and tribological tests [11,18–22]. Although lab tests (pin-on-disk, four-ball, copper corrosion, etc.) provide evidence and insights into lubricants' performance, it is challenging to evaluate engine conditions in the laboratory [18,22,23]. In fact, it has been shown that elaborate tests fail to reproduce the tribofilms observed in engine parts [18,21]. Furthermore, lab tests often do not evaluate lubricant degradation over time and its impact on system performance [22]. This situation is aggravated for motorcycle engines since in this application the oil also lubricates the gearbox and the clutch [12,13,24]. Consequently, many lab studies are often disregarded when it comes to attesting to the efficiency of aftermarket additives.

In order to cover this gap, experimental work was proposed to evaluate metal conditioner's response in laboratory tests and in field tests using two new motorcycles of low displacement. The lab tests aimed to evaluate the friction and wear response of metallic parts lubricated with engine oils with and without metal conditioner. The field study encompassed fuel consumption monitoring, oil analysis, and a wear evaluation of engine and transmission systems parts.

In Sections 2 and 3, the laboratory tribotests are presented first, followed by the field tests. The field test description and results are separated into oil analysis, wear analysis and fuel economy. Finally, the discussion and conclusion sections integrated lab and field results to highlight the noteworthiness of field studies.

2. Materials and Methods

Field studies are costly and time-consuming. Therefore, prior to field studies, tribotests were performed to verify the potential of metal conditioners to reduce wear.

2.1. Laboratory Tests

Tribotests were performed using a CETR-UMT-2MT s/n T1471 (Bruker, Massachusetts, USA) model with a sphere-plane configuration in the reciprocating mode. The reciprocating motion was set with a 10 mm stroke, 5 Hz frequency, and normal load of 50 N. The moving body was a 10 mm diameter ball bearing of AISI 52100 steel, and the static flat surface was made of AISI 4140 steel quenched and tempered ($HV_{0.1} = 360 \pm 30$), which is often used for gears and crankshafts. The contact surface was ground to P220 SiC paper with a unidirectional texture pattern, similar to what is observed in gear teeth. Tests were performed at 40 °C and 80 °C with abundant lubrication (15 mL) with the sphere sliding across the surface lay. The commercial engine oil advised for use in the studied motorcycles SAE 10W-30 API SL JASO MA, and its mixture with MC in a proportion of 25:1 mL, were tested three times each. The lateral forces and coefficient of friction were recorded automatically during the test.

After the tribotests, the tribo-counterparts were cleaned in hexane and then acetone in an ultrasonic bath for 10 min each. The wear volume of the block (static part) was computed based on 3D measurements (Taylor Hobson, New Star Road Leicester, UK, Talysurf CCI Lite M12-3993-03, white light) of the wear track following the procedure described by Ayerdi et al. [25]. In brief, the 3D topography of the wear track and surrounding plane surface was measured. Then, the mean plane was defined based only on the non-affected area. Finally, the wear volume was calculated using the "measurement of a wrinkle" tool from TalyMap[®], which calculates the volume below the mean plane within the contour drawn by the user. The advantage of this method is limiting the area of interest, and therefore minimizing the computation of the valleys of the unworn surface area on the wear volume calculation [25]. The wear volume of the sphere was computed based on 3D measurements of the wear and its surroundings. Then, the form of a $\emptyset 10$ mm sphere was subtracted from the original measurement. Finally, the wear volume was calculated using the "Volume of a peak/hole" tool from TalyMap \mathbb{R} . Figure 1 shows typical wear marks of the block and the sphere along the contour drawn by the user. Making the contour broader barely changes the contact area since the vicinity of the contact has an average value of zero.



Figure 1. Wear volume measurement of a wear track on the flat (**a**) and sphere (**b**) specimen using 3D profilometry.

The selected operating conditions led to a maximum Hertzian pressure of $P_0 \approx 1400$ MPa and maximum specific film thickness of $\Lambda \approx 0.2$. The calculations are detailed in a previous work [20]. This situation is similar to that observed at the beginning of tooth gearing, in which high levels of sliding occur [26]. Furthermore, boundary lubrication ($\Lambda < 1$), high contact pressure, and sliding motion across the texture direction are ideal conditions to test additives' performance [20,21,27], particularly anti-wear and extreme pressure additives,

which are the main constituents of most aftermarket additive packages for engine oils [1,9]. Under these conditions, metal contact under higher stress occurs, leading to asperity deformation and wear, which in turn trigger the additives [23]. Tables 1 and 2 summarize the main lubricant and material properties, respectively.

Table 1. Lubricant properties.

Properties	ASTM Standard	Unity	SAE 10W-30 API SL JASO MA	Mixture 10W-30 + MC (25:1)
Kinematic Viscosity at 40 °C	ASTM D445 [28]	cSt	69.79	65.36
Kinematic Viscosity at 100 °C	ASTM D445 [28]	cSt	10.32	9.575
TBN	ASTM D4739 [29]	mg KOH/g	7.55	7.09
TAN	ASTM D974 [30]	mg KOH/g	0.31	0.44

Table 2. Tribological test material properties.

	Ball	Block
-	AISI 52100	AISI 4140 Tempered and quenched
-	HRC = 60-66	$HV_{0.1} = 360 \pm 30^{\circ}$
GPa	210	210
-	0.30	0.30
MPa	7350	3531
m	$5 imes 10^3$	∞
m	$5 imes 10^3$	∞
μm	0.05 ± 0.01	0.60 ± 0.07
	- GPa - MPa m m m	$\begin{tabular}{cccc} \hline Ball \\ \hline - & AISI 52100 \\ - & HRC = 60-66 \\ \hline GPa & 210 \\ - & 0.30 \\ \hline MPa & 7350 \\ \hline m & 5 \times 10^3 \\ \hline m & 5 \times 10^3 \\ \hline \mu m & 0.05 \pm 0.01 \\ \hline \end{tabular}$

2.2. Field Tests

Two new motorcycles (0 km) with low displacement (160 cm³), model Honda Titan 2019, were purchased specifically for this study. Their performance was monitored from 0 km to 15,000 km regarding lubricant conditioning, engine parts dimension (wear), and fuel consumption. Both motorcycles were used in typical urban driving conditions. The drivers were not informed about which motorcycle was lubricated with metal conditioner. Furthermore, the motorcycles were randomly driven by the drivers until reaching a mileage of 7500 km. For the remaining miles (from 7500 to 15,000 km) each motorcycle was exclusively driven by one driver. The motorcycles were always supplied with gasoline without additives at the same gas station. The fuel consumption was monitored and recorded during the 15,000 km. Once a week, the front tires were calibrated at 25 psi and the rear tires at 29 psi.

Specialized company services were hired to perform a used-oil analysis and powertrain pieces measurements. This decision contributed to the reliability of the results for the following reasons: it divided the large volume of the field test, increased reliability, and avoided biased measurements. Other actions taken to minimize experimental errors are detailed in the following sections. The procedure used to evaluate the oil condition, wear and fuel consumption is summarized in Figure 2.

2.2.1. Oil Analysis

An external company performed all lubricant analyses following the American Society of Testing Materials (ASTM) procedures listed in Table 3. The crankcase of Motorcycle B was always filled with the following recommended engine oil: SAE 10W-30 API SL JASO MA. Motorcycle A received a mixture of lubricating oil and metal conditioner in the proportion of 25:1 (1 L of oil + 40 mL of conditioner) during the oil changes at 1000, 7000, and 14,000 km. In the remaining changes, only the recommended oil was used.



Figure 2. Field Study Flowchart.

Table 3. Lubricants analysis techniques.

Analysis	Feature	Unit	Standard
	Kinematic Viscosity at 40 $^\circ C$ and 100 $^\circ C$	cSt (centistokes)	ASTM D445 [28]
	Viscosity Index (VI)	Dimensionless	ASTM D2270 [31]
Physico-chemical	Merit of Dispersancy, Contamination Index, Weighted Demerit	Dimensionless	ASTM D7899 [32]
and degradation	Precipitation Number	Dimensionless	ASTM D91 [33]
	Total base number (TBN)	mg KOH/g	ASTM D4739 [29]
	Total acid number (TAN)	mg KOH/g	ASTM D974 [30]
	IR Spectroscopy (FTIR)	Abs/cm (absorbency/cm)	ASTM D7889 [34]
	Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)	ppm (parts per million) < 5 μm	ASTM D5185 [35]
Wear metal particles	Microscopic Characterization	Dimensionless: Soot/oxidation products, Silicon dioxide, >5 μm Iron alloy particles < 15 μm	ASTM D7684 [36]

SAE 10W-30 API SL JASO MA **Metal Conditioner** Mixture 25:1 1.15 0.1 * 0.81 Fe (ppm) 3.02 0.1 * 6.96 Si (ppm) 879.7 Zn (ppm) 2.51 817.5 Sn (ppm) 0.1 * 0.420.1 * Ca (ppm) 1746 2.851604 Na (ppm) 586.5 0.1 * 524.5 B (ppm) 454.80.1 * 421.6 Mg (ppm) 20.330.1 * 18.67 1021 852.1 978.8 P (ppm) 0.1 * 49.89 54.13 Ti (ppm)

The elementary composition of the lubricants is given in Table 4.

 Table 4. Multielement determination (ppm) of fresh lubricants by ICP-AES (ASTM D5185 [35]).

 SAE 10W-30 API SL JASO MA Metal Conditioner Mixture 25:1

* Element content at 0.1 ppm corresponds to the equipment's lower detection limit.

The protocol followed for sampling was as follows: (1) The motorcycle was started for 5 min to ensure the recirculation of the engine oil throughout the engine. (2) A disposable hose was inserted at the inlet hole of the oil level verification rod. (3) The hose was inserted halfway up the tank, and the oil was extracted with an oil-sampling vacuum pump. (4) Two bottles of 200 mL were filled with used oil to carry out the analyses indicated in Table 3. The remaining oil (~600 mL) was allowed to drain until the crankcase was emptied.

The oil changes and sampling were performed in the approximate mileages of 1000, 4000, 7000, and 10,000 km, as indicated in Figure 2. Between 10,000 and 15,000 km, the oil was changed every 1000 km. However, oil analyses were performed only in the last mileage of ~15,000 km. The automaker suggested different oil change intervals which were as follows: the first one at 1000 km, the second at 6000 km, and then every 6000 km. This suggestion was not followed because most motorcycle users do not follow this recommendation (dealers, delivery). The evaluation of MCs' effect for longer oil change intervals is within the scope of future work.

2.2.2. Wear Analysis in the Main Engine Parts

The pieces were measured at the beginning (0 km) and at the end of the field study (15,000 km); therefore, the engines were disassembled twice. An experienced external company measured the parts presented in Table 5. The transmission roller chain was removed for cleaning with kerosene and finally mounted and lubricated during every fuel supply. In the case of Motorcycle B, the lubrication was performed solely with the Aerosol grease (REPSOL, São Paulo, Brazil, MOTO CHAIN DRY). In the case of Motorcycle A, after cleaning the chain, the metal conditioner was applied with a sponge. Then, the chain was heated at 80 °C, and finally, it was lubricated with the aforementioned grease.

Motorcycle A parts were dipped in the metal conditioner for 90 min in an ultrasonic bath at 80 °C prior to the motor assembly. Motorcycle B parts received no additional treatment; only the recommended engine oil was used prior to assembly. At the end of the test, some pieces of Motorcycle B had to be exchanged to ensure its proper functioning due to severe wear. These pieces were Gear #5 (secondary axis) and the transmission kit (crown, pinion, and roller chain). The piston rings, gear #5, crown and pinion were observed in the stereoscopic microscope (Olympus, Shinjuku City, Tokyo, SZX10 Series) to detail the wear mechanisms and severity. A scanning electron microscope equipped with energy dispersive X-ray spectroscopy (SEM-EDS: Zeiss, Oberkochen, Germany, EVO MA15) was used to investigate the elemental composition of the tribofilms formed on the surface of those pieces.

Part	Dimension	Description of the Measurement Procedure
Cylinder *	Cylinder top, center and base $Ø$	In two transverse directions
Piston **	Piston skirt $Ø$	At standard 10 mm height, perpendicular to the surface of the piston.
Primary axis ***	Axis Gear Ø (14 teeth) Gear #1 Ø (23 teeth) Gear #2 Ø (24 teeth) Gear #3 Ø (20 teeth) Gear #4 Ø (30 teeth)	Two rollers of \emptyset 3.475 mm at each end Two rollers of \emptyset 2.968 mm at each end Two rollers of \emptyset 3.475 mm at each end Two rollers of \emptyset 3.475 mm at each end Two rollers of \emptyset 2.968 mm at each end
Secondary axis ***	Gear #1 \emptyset (39 teeth) Gear #2 \emptyset (32 teeth) Gear #3 \emptyset (26 teeth) Gear #4 \emptyset (22 teeth) Gear #5 \emptyset (39 teeth)	Two rollers of \emptyset 3.475 mm at each end Two rollers of \emptyset 2.968 mm at each end Two rollers of \emptyset 3.475 mm at each end Two rollers of \emptyset 3.475 mm at each end Two rollers of \emptyset 2.968 mm at each end
Chain roller ***	Pitch distance and roller diameter.	The chain was fastened on a fixed walrus with the help of a metal rod.
Crown ***	Ø (44 teeth)	Two rollers of Ø8.462 mm at each end
Pinion ***	Ø (15 teeth)	Two rollers of Ø8.462 mm at each end

Table 5. Procedures for measuring powertrain pieces (Ø: diameter).

Measurement instrument and its accuracy: * Dial bore gauge (0.1 µm); ** Digital micrometer (1 µm); *** Caliper (5 µm).

2.2.3. Analysis of Fuel Economy

Fuel economy results (km/L) were statistically evaluated (95% confidence) using the Matlab[®] Software (Academic License number 31568410) Analysis Tool: Two-Way Analysis of Variance (ANOVA) for unbalanced design. This analysis tested the null hypothesis of whether the averages between motorcycles were equal and revealed the effects of different factors or variables. In this case, the ANOVA analysis estimated the relationship between two factors at a time (motorcycle vs. driver, motorcycle vs. regime), with each factor consisting of several levels (conditions).

For example, the "motorcycle" factor had the following two levels: "Motorcycle A" and "Motorcycle B". The "regime" factor had the following 3 levels: "0k to 1k", "1k to 10k" and "10k to 15k", while the "driver" factor had the following 2 levels: "random" and "unique". The implemented analysis of variance also evaluated the independent effect of each factor on fuel consumption.

3. Results

3.1. Tribological Tests

Tribotests were evaluated based on the COF curves, and the wear volume of the blocks and the spheres. Figure 3 shows the coefficient of friction versus the test time at the temperatures of 40 $^{\circ}$ C and 80 $^{\circ}$ C for the 10W-30 and the mixture. The friction curves represent the average of three tests.

Table 6 presents the mean and standard deviation values for the COF and wear volumes of the blocks and the spheres. The analysis shows that the addition of metal conditioner into the SAE 10W-30 clearly led to a reduction in the COF and wear at both tested temperatures. It also shows the wear volume of the sphere was at least two orders of magnitude lower than the wear of the blocks, as expected due to its greater hardness (Table 2). This indicates the metal conditioner improved the lubricant performance at the tested conditions and therefore might be a good asset to the 10W-30 lubricant. However, as mentioned in the introduction, engine lubricants must present more attributes than just wear and friction reduction. For instance, they must keep their properties, not oxidize and prevent corrosion during their service life [13,24]. Furthermore, the tribotests do not faithfully represent the contact conditions and materials observed in the combustion engine.

These characteristics of the mixture were evaluated in a field study and are presented in the following sections.



Figure 3. Coefficient of friction of the last 1200 s at the tribological tests conditions ($P_0 = 1400$ MPa, 5 Hz, dip lubrication, 10 mm stroke length).

Table 6. Tribological tests results.

	40	°C	80 °C		
	10W-30 Mixture		10W-30	Mixture	
Block scar wear volume (mm ³)	0.0118 ± 0.0033	0.0063 ± 0.0023	0.0177 ± 0.002	0.015 ± 0.0006	
Ball wear volume (µm ³)	$36,\!132 \pm 1995$	$30,092 \pm 12,882$	$138,\!932 \pm 16,\!459$	$56,\!525 \pm 18,\!518$	
COF	0.095 ± 0.0022	0.0913 ± 0.0025	0.1013 ± 0.0031	0.0967 ± 0.0021	

3.2. Field Tests

3.2.1. Physico-Chemical and Degradation Oil Analysis

The evolution of TAN, TBN, and dispersancy along the field study is shown in Figure 4a. It is important to point out that the TAN and TBN values of the fresh 10W-30 oil and its mixture with metal conditioner (25:1) (10W-30 + MC) are clearly different. In the first oil change (1000 km), oil A (Motorcycle A) and oil B (Motorcycle B) presented the same TAN value, but the increase in the acidity of oil B was higher. In terms of basicity, the reduction in TBN in the first 1000 km was similar for both oil samples compared to their respective fresh values. In the successive oil changes, TAN and TBN differences between the motorcycles were higher than their initial differences. Therefore, it is evident from Figure 4a, that Motorcycle A, in which metal conditioner was added, always presented higher TAN and smaller TBN values from the first oil change (>1000 km).

The evolution of TAN and TBN shown in Figure 4a suggests a greater tendency for oil to acidify (amount of thermal oxidation and contamination with combustion by-products) accompanied by a drop in alkaline reserves (compounds that neutralize acid products) on Motorcycle A. According to the laboratory that performed the oil analysis, all TAN and TBN values presented in Figure 4a are within the acceptable operating range. This is in agreement with the "warning limits" defined by several researchers [12,37–39] and summarized by Booser [40]. However, it is important to mention there are no universally accepted warning limits as different investigators and operating conditions may suggest different limits for a given oil [37–39,41].



Figure 4. (a) Evolution of Total Acid Number (TAN), Total Base Number (TBN) and Merit of dispersancy values based on mileage and motorcycle. TAN values were not determined in the last samples (15,000 km). (b) Evolution of kinematic viscosity at 40 °C and 100 °C based on mileage and motorcycle. * Indicates the oil changes in which the engine A received the mixture of oil + MC.

The dispersancy of the oils did not present significant differences between both motorcycles and was always higher than 85% (0.85), as seen in Figure 4a. In addition, the other evaluated physico-chemical properties remained unchanged along the test and at its minimum value, and were as follows: Contamination Index = 0.1; Precipitation Index = 0.05; Weighted loss = 1–2. The evolution of viscosity with mileage is presented in Figure 4b. The kinematic viscosity at 40 °C and 100 °C of used oils presented variations of below 15% compared to the value of fresh oil or mixture, which indicates little variation in these properties between the motorcycles and the intervals between oil changes [37,38,40,42].

Fourier transform infrared spectrometry (FTIR) is one of the most common methodologies used to measure oil degradation in used engine oils. FTIR identifies the presence of organic compound products of oxidation, nitration, and oil sulfation reactions. Figure 5a shows the absorbance values (abs/cm^{-1}) of the characteristic degradation bands according to ASTM D7889 [34] for the fresh 10W-30 oil and its mixture with the metal conditioner. It is clear that the fresh mixture has significantly higher nitration, oxidation, and sulfation values compared to fresh 10W-30 oil. It is important to note that the higher absorbance values of the fresh mixture (Figure 5a—Fresh Mixture) do not indicate oil degradation. Instead, it reveals a characteristic of the metal conditioner, i.e., it contains organic compounds with infrared absorbance in the oxidation (1800 to 1670 cm^{-1}) and sulfation (1180 to 1120 cm⁻¹) regions, and possibly sulfur-containing and oxygen-containing base oil additives. Another standard for monitoring in-service lubricants (ASTM E2412 [43]) highlighted that several additives, such as detergents, dispersants, antioxidants, and others of the formulation package, can generate significant absorbances in the conditioning monitoring regions of interest. In particular, chemical compounds containing the carbonyl group (C=O), such as esters, ketones, aldehydes, and carboxylic acids strongly absorb in the oxidation region [44]. Therefore, the indiscriminate evaluation of infrared spectra can lead to imprecise conclusions.

Figure 5b–d show the percentage variation of nitration, oxidation, and sulfation of the used oils in comparison to the corresponding fresh ones, respectively. In the case of Motorcycle A, the percentage variation at 4k and 10k oil changes were calculated based on the fresh mixture; in the remaining ones, the fresh oil values were considered. Thus, it follows from Figure 5b that the nitration of the used oil A (Motorcycle A) maintained lower values than the used oil B, except in the last oil change. On the other hand, it is observed in Figure 5c,d that the oxidation and sulfation percentage changes for the used oil from Motorcycle A were very unstable. For the 1k, 7k, and 15k oil changes, the oxidation and sulfation values of Motorcycle A surpassed those of Motorcycle B. However, the opposite trend occurred at 4k and 10k, making it difficult to reach a conclusion. This analysis is complex because the metal conditioner might not be completely adsorbed on the metal surfaces. Thus, part of the metal conditioner (as well as the oil additives) remains in the crankcase oil as a reserve for gradual consumption over time. This hypothesis would explain why in the 4k oil change, the oxidation and sulfation percentage changes were negative, as all of the metal conditioner had been consumed in 3000 km of operation.





Based on these results, the properties of the used oils of both motorcycles remained within the acceptable limits of alkaline reserve levels and acid number, cleaning, and suspension of pollutants, nitration, and viscosity over the service life. With regard to FTIR oil degradation analysis, the addition of metal conditioner into 10W-30 oil generated interferences in absorbance spectra in the oxidation and sulfation regions, increasing their values. These results are in agreement with the advertising of metal conditioner formulators [5–8] without suggesting they improve the physico-chemical properties of engine oils. Infrared degradation analyses should be evaluated with caution because the presence of certain additives (possibly esters) does not allow for a direct comparison between lubricants with and without metal conditioner.

3.2.2. Wear Metals Analysis in Used Oils

Table 7 presents the contents of wear metals (ppm) along the 15,000 km estimated using ICP-AES spectrometry. This technique cannot quantify particles larger than 5 µm, and therefore we only evaluated particles typical of mild wear and corrosion. The content of other metals associated with wear, such as chromium and nickel, was found at the equipment's lower detection limit (0.1 ppm), and was thus classified as insignificant. The motorcycles did not have the exact same mileage (km, service time) at each oil change, so Table 7 presents the absolute (ppm) and the standardized values (ppm/km). Table 7 also illustrates conservative warning limits for each element based on the current literature [37,38,40,42].

Cumulative Mileage (km)		Mileage between	Alun	ninum	Copper		Iron **		Silicon **	
		Oil Change	ppm	ppm/km	ppm	ppm/km	ppm	ppm/km	ppm	ppm/km
	-	Fresh mixture	0.1	-	0.1	-	0.81	-	6.96	-
	-	- Fresh oil 10W-30	0.1	-	0.1	-	1.15	-	3.02	-
	1040 *	1040	48.63	0.0468	21.85	0.0210	67.76	0.0652	29.09	0.0280
	4005	2965	56.75	0.0191	17.33	0.0058	75.28	0.0254	19.71	0.0066
NG / 1	7013 *	3008	39.07	0.0130	27.36	0.0091	47	0.0156	14.01	0.0047
Motorcycle	10,199	3186	60.66	0.0190	20.58	0.0065	82.44	0.0259	12.66	0.0040
А	14,070 *	-	-	-	_	-	-	-	_	-
	14,977	907	11.46	0.0126	0.1	0.0001	20.66	0.0228	-0.28	-0.0003
		Total (ppm)	216.57	_	87.22	_	293.14	_	75.19	_
	969	969	56.26	0.0581	18.65	0.0192	84.06	0.0867	37.84	0.0391
	4029	3060	77.98	0.0255	12.99	0.0042	88.22	0.0288	25.78	0.0084
Motorcycle	7022	2993	62.84	0.0210	7.91	0.0026	58.11	0.0194	16.78	0.0056
В	10,033	3011	67.96	0.0226	8.71	0.0029	64.66	0.0215	16.85	0.0056
	14,048	-	-	-	_	-	-		_	
	14,961	913	11.15	0.0122	0.1	0.0001	15.68	0.0172	11.66	0.0128
		Total (ppm)	276.19	-	48.36	-	310.73	-	108.91	-
Warning L	imits ***		>30		>40		>100		>30	

Table 7. Wear metals (ppm and ppm/km) in the used-oil analysis (the highest values between the motorcycles are highlighted in yellow).

* Indicates the oil changes in which the engine A received the mixture of oil + conditioner. ** The iron and silicon content of the fresh oil or mixture was subtracted from the values of each used oil. *** According to [37,38,40,42].

The fresh 10W-30 oil and its mixture with the metal conditioner presented iron and silicon in their formulation (Table 7 (**)). Therefore, the absolute values (ppm) in the used oil (Table 7) were corrected by subtracting the contents of these elements from the new condition. In the mileages indicated with *, the crankcase of Motorcycle A received the mixture with metal conditioner. Hence, in the used oil samples for 4k, 10k, and 15k, the values (Fe, Si) were corrected by the fresh mixture, and during rest, by the fresh 10W-30 oil.

The levels of copper and iron were below the warning limits established in the literature for both motorcycles, while the level of aluminum was above, and the level of Silicon was slightly higher for the first oil change of Motorcycle B. Considering the oil was changed at intervals smaller than those recommended (<6000 km), aluminum values above the warning limits were not expected. In fact, for Motorcycle B, the aluminum content was up to 2.6 times higher than the warning limits.

Table 8 presents the percentage differences in the content of elements (ppm/km, Table 7) between the motorcycles. The results of Tables 7 and 8 show that in Motorcycle A, the initial application of the metal conditioner (engine assembly) decreased the amount of aluminum and iron wear metals (ppm/km) in the first 7000 km of engine break-in. In the case of aluminum, its content was lower until 10,000 km, but towards the last mileage point, it was approximately equal to Motorcycle B. With respect to iron content, Motorcycle A presented values up to 20% and 33% higher than Motorcycle B in the last two mileages; however, over the 0–15,000 km, Motorcycle A had a smaller quantity of ferrous particles (Table 7: Total (ppm) = 293.14). Regarding copper, the used oil A presented a higher quantity until 10,000 km, but similar values in the last oil change (15,000 km). It is important to keep in mind that during the service time between 10,000–15,000 km, oil change intervals were 1000 km (although the manufacturer recommends oil changing at every 6000 km); however, only the last oil change was sampled and analyzed (15,000 km). So, the final used-oil analysis (15,000 km, ppm/km, Table 7) suggests that the addition of metal conditioner for a short oil interval (1000 km) did not bring significant gains in the protection of aluminum and copper parts while it led to 33% higher iron wear, although still within the warning limits.

Motorcycle A vs. Motorcycle B: $(\frac{\frac{ppm}{km}(A)}{\frac{ppm}{km}(B)}-1) \times 100\%$						
Oil Change	Aluminum	Copper	Iron	Silicon		
1000 *	-19%	+9%	-25%	-28%		
4000	-25%	+38%	-12%	-21%		
7000 *	-38%	+244%	-20%	-17%		
10,000	-16%	+123%	+20%	-29%		
15,000	+3%	+1%	+33%	-2%		

Table 8. Comparative resume of the content of elements (%) between motorcycles (A versus B).

* Indicates the oil changes in which the engine A received the mixture of oil + conditioner.

The size of the particles in the oil samples is a limitation of the ICP-AES spectroscopy technique (ASTM D5185 [35]). Sizes greater than 1 μ m up to 8 μ m, depending on the element, may not be detected because the plasma cannot completely atomize the particles [45]. This depends on the oil dilution in solvents and on the suspension/settlement of the particles according to their atomic weight and density [45]. Thus, the particle morphology was examined in the oil samples according to the ASTM D7684 [36] standard using the filter patch analysis technique. The results of the soot and oxidation products were classified as typical for all used oil samples. Concerning the presence of ferrous particles with sizes between 5–15 μ m, only the first oil change (1040 km) of Motorcycle A showed large particles. The remaining used oil samples did not show ferrous particles (5–15 μ m) for both motorcycles. In other words, the differences in the iron content present in the used oil between the motorcycles were solely on the micrometric particles of <5 μ m sizes, which are related to mild and corrosion wear, as shown in Table 7.

The motorcycles (Honda Titan 2019) use a single lubrication system for the engine and the transmission system, so the oil poured into the crankcase lubricates all the parts involved. Consequently, the wear metals derive come from the components of the whole power unit. For instance, the aluminum particles are most likely derived from the wear of the piston, while the primary source of copper is likely a result of the rod needle bearing cage coating. In the case of iron, the connecting rod, the cylinder bore, the crankshaft, the gears, and the primary and secondary axes were the main lubricated parts made of steel. All engine and transmission system components will continue to be used on these motorcycles, except the transmission kit and gear #5 of the secondary axis, for reasons that will be explained in the next section.

3.2.3. Wear Analysis in the Main Engine Parts

Table 9 contains the results of the engine and transmission system components. The dimensional differences in the parts after 15,000 km are presented as a percentage based on the measurements of the new part (0 km). Thus, it is observed that most pieces changed their dimensions due to the system's break-in period in both motorcycles. It is important to emphasize that those dimensional variations are not directly related to the formation of debris because part of it is related to parts deformation (without material removal). Thus, Tables 7 and 9 are not directly related. Furthermore, dimension differences of less than |0.05%| are hardly representative. Consequently, only the most significant dimensional variations (>|0.05%|) between motorcycles A and B were highlighted and will be further discussed. Crown, Pinion, Gear #2, and Gear #5 presented unequal measures between the teeth, so the results are presented as a range of values.

	Motorcycle A	Motorcycle B
Cylinder top Ø	0.0174%	0.0174%
Cylinder center Ø	0.0279%	0.0288%
Cylinder base $Ø$	0.0410%	0.0349%
Piston skirt Ø	-0.021%	-0.017%
Chain Roller Ø	-0.826%	-1.004%
Chain pitch distance	0.912%	1.484%
Crown Ø	-0.0482% to $-0.0429%$	-0.0643% to $-0.0589%$
Pinion Ø	-0.331% to $-0.302%$	-0.374% to $-0.359%$
Primary axis Ø	0%	0%
Gear #1—Primary axis Ø	0%	0%
Gear #2—Primary axis Ø	-0.0733% to $-0.0367%$	-0.0184%
Gear #3—Primary axis Ø	-0.0215% to $0%$	-0.0215% to $0%$
Gear #4—Primary axis Ø	0%	-0.0098%
Gear #1—Secundary axis Ø	0%	0%
Gear #2—Secundary axis Ø	-0.0092%	-0.0185%
Gear #3—Secundary axis Ø	-0.0257%	-0.0171%
Gear #4—Secundary axis Ø	-0.0099%	0%
Gear #5—Secundary axis $Ø$	-0.031% to $-0.015%$	-0.170% to $-0.015%$

Table 9. Relative change (%): In yellow, the highest values between the motorcycles are highlighted. Differences greater than $\pm 0.05\%$ were considered less representative.

The results of Table 9 indicate that the wear of the piston, cylinder, and most of the pieces of the transmission system were not relevant (<10.05%1) in both motorcycles after 15,000 km. The wear of iron components was moderate and less worrying in most pieces except in the cells highlighted in yellow in Table 9. These results show that a complete wear analysis should encompass multiple complementary techniques as was developed in this work (ICP-AES, particulate analysis, parts measurement, and visual inspection). Complementary information could be provided by analytic and direct ferrography, which will be in the scope of future analysis. Nevertheless, Motorcycle B's transmission kit (crown, pinion, and roller chain) showed significant dimensional changes for all its elements in comparison to Motorcycle A. In fact, the chain of Motorcycle B broke at 14,961 km, thus finalizing the field study. The chain of Motorcycle A completed the test without any issue. Thus, all the components of the transmission kit of Motorcycle B will need to be replaced by a new one to guarantee its operation.

The changes presented in Table 9 are direct measures of macroscopic wear and/or deformation, but they do not represent severe conditions that prevent or disturb the motorcycle's correct functioning. In fact, all pieces will continue to be used in these motorcycles, except the transmission kit and gear #5 of the secondary axis, both from Motorcycle B. To understand the significant differences in the crown, pinion, and gear #5, and the less representative differences in other components (cylinder bore), some pieces were characterized by conducting stereoscopic microscopy and an SEM-EDS analysis. The results are shown in Figures 6–10.



Figure 6. SEM micrograph and EDS-mapping of the oil control ring of Motorcycle A (**a**,**c**) and Motorcycle B (**b**,**d**).



Figure 7. SEM micrograph and EDS-mapping of the oil ring expander of the Motorcycle A (**a**,**c**) and Motorcycle B (**b**,**d**).



Figure 8. Optical macrograph of the crown of Motorcycle A (**a**) and Motorcycle B (**b**). SEM micrograph (**c**,**d**) showing the regions where EDS analysis was performed for crown A (**c**) and crown B (**d**). Element weight percent results from EDS analysis (**e**,**f**). Substrate alloy elements (Al, Si, Mn, Fe), oxygen and carbon were excluded from the EDS-table for comparative purposes.



Figure 9. Optical macrograph of the pinion of Motorcycle A (a) and Motorcycle B (b).



Figure 10. Optical macrograph of the Gear #5 of Motorcycle A (**a**,**c**) and Motorcycle B (**b**,**d**). Teeth with moderate to destructive wear (**a**,**b**) and teeth with light wear (**c**,**d**). SEM micrographs (**e**,**f**) showing the regions where EDS analysis (wt.%, **g**,**h**) was performed for the teeth (**c**,**d**), respectively. Substrate alloy elements (Cr, Si, Mn, Fe), oxygen and carbon were excluded from the EDS-table for comparative purposes.

Piston Rings

Worn surfaces of the compression, middle and oil control rings from both motorcycles presented similar wear mechanisms, which are typical of mild sliding wear with two and three-body abrasion, as observed by surface smoothening, vertical scratches and indentations [21,27,46]. Adhesion and corrosion, which are usually observed in piston rings, did not play a significant role. The abrasive wear was mostly caused by hard particles originating either from the combustion process or as a product of wear itself [46]. The SEM images of the oil control ring presented in Figure 6a,b depict quite well the aforementioned wear mechanisms. In short, SEM images did not reveal any difference in the wear level of the piston ring lubricated with 10W-30 and that lubricated with the mixture.

Along with the SEM images, Figure 6c,d also present the EDS spectra of some chemical elements. The goal of these images is to show that the chemical elements of both lubricants are spread all over the surface, with a higher concentration at the bottom, due to lubricant accumulation in that part during operation. However, the chemical elements observed in each ring were different. While calcium, phosphorus, sulfur and zinc were detected in the piston rings from Motorcycle B, as observed by many scholars [21,27,46], the piston

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ring from Motorcycle A presented only calcium. The lack of the other chemical elements from the 10W-30 engine oil on the piston rings from Motorcycle A clearly indicates the metal conditioner formulation has a synergic effect with the engine oil and alters tribofilm formation and composition. In this specific case, the changes did not bring any visible advantage or disadvantage.

The oil ring expander also presented deposits that are likely to consist of a mixture of metal oxides with lubricant and combustion products [47], as shown in Figure 7a,b. Both piston rings presented oxygen, calcium, phosphorus, sulfur and zinc spread relatively evenly and in a similar fashion across the piston ring contacting surfaces. EDS maps of some of the elements are shown as an example (Figure 7c,d). Besides that, the piston ring from Motorcycle A also presented chlorine, which is part of some metal conditioners' composition [4], as confirmed by Coppini et al. [17].

Crown and Pinion (Chain Transmission)

Figure 8a,b show the crown's surface where the primary contact with the roller's chain occurred. A larger worn area in the crown of Motorcycle B (Figure 8b) was observed, which is in agreement with the smaller diameters of both the crown and the chain rollers (Table 9). Additionally, more intense abrasive wear was observed in crown B (Figure 8b) compared to crown A (Figure 8a). EDS analyses (Figure 8c–f) showed that both piston rings presented oxygen, calcium, phosphorus, sulfur, magnesium, titanium, and zinc patches all over the crown contacting area. Besides that, chlorine was detected in the piston ring of Motorcycle A, as also observed for the piston rings.

Motorcycle pinions exhibited mild abrasive wear, possibly due to the rolling–sliding contact with the rollers of the chain, localized in the addendum region of the teeth faces, as shown by the red square in Figure 9a,b. In addition, some pinion teeth exhibited surface oxidation in Motorcycle A (black arrow in Figure 9a). Such oxidation is due to the careless storage of the samples that did not present oxidation after disassembly. SEM + EDS analyses of the region identified the presence of sulphur, highlighted by the red rectangle, in the pinion of Motorcycle B, and sulphur, calcium and sodium in Motorcycle A. The micrograph evaluation of the pinions did not reveal any visible differences in wear severity.

Gears

Among all gears of the transmission system of both motorcycles, the #5 gears were the only ones with visible wear to the naked eye, as observed in Figure 10. Gear #5 of Motorcycle A presented moderate wear on some teeth (Figure 10a) and light wear in others (Figure 10c), while that of Motorcycle B showed severe (Figure 10b) and light wear (Figure 10d). Both gears #5 exhibited micropitting in the addendum region identified by the red arrows in Figure 10a–d. Additionally, both gears #5 showed another type of micropitting in the dedendum region, specifically in an area slightly below the pitchline (yellow arrows in Figure 10a–d). This type of pitting is called frosting wear due to the surface finish that is generated. The most worn gear #5 teeth in Motorcycle A exhibited destructive pitting (Figure 10a). However, gear #5 of Motorcycle B suffered from destructive macropitting (spalling wear) with more severe and in-depth material removal, as observed in Figure 9b.

Figure 10e,f show the SEM images with the identification of the areas where an elemental chemical analysis was performed. SEM + EDS analyses were performed on several teeth of the gears from Motorcycle A and B (Figure 10g,h). In all cases, the same chemical elements were detected, although Motorcycle B presented them consistently in higher percentages.

In short, the dimensional changes of some powertrain pieces (Table 9) and their visual inspection demonstrated different macroscopic wear levels between the motorcycles. This suggests that some wear particles were larger than those detected with ICP-AES. These particles should have been observed in the ASTM D7684 analyses since particle precipitation at the bottom of the crankcase should not have occurred since the engine was

started before the oil sampling to avoid this issue. However, the reported levels of larger particles were within the warning limits. Complementary information could be provided by analytic and direct ferrography, which is in the scope of future analysis.

Besides that, the results elucidated that the lubrication of the transmission kit (crown, pinion, and roller current) with metal conditioner ensured minor wear and longer service time. In addition, under conditions of high contact pressures and cyclic loads (fatigue) undergone by the gears, the metal conditioner significantly increased wear resistance, as seen in gear #5 (Figure 10a,c).

3.2.4. Analysis of Fuel Economy

Fuel economy (FE) or fuel efficiency was evaluated using an analysis of variance (ANOVA). The results are presented in Figure 11. In the ANOVA table (Figure 11a), X1, X2, and X3 correspond to the factors 'Motorcycle', 'Driver' and 'Regime', respectively. Regime is the time between oil changes, which were 1000 km and 3000 km. The terms marked with # are not full rank. The *p*-value 'Prob > F' > 0.05 (confidence of 95%) of each factor (X1, X2, X3) indicates that their means are not significantly different from each other. Additionally, the last three entries are the *p*-values for the two-way interactions, represented by X1*X2, X1*X3, and X2*X3. The *p*-value > 0.05 indicates that the interaction between the two factors is insignificant in terms of fuel efficiency. It confirms the null hypothesis that there are no differences in FE related to the interaction between the different factors. In short, the multiway analysis of variance revealed that the application of metal conditioner, the changes in the driver, and the oil interval did not produce differences in fuel economy that are statistically significant.

a Analysis of Variance						
	Source	Sum Sq.	d.f.	Mean Sq.	F	Prob>F
	X1	19.54	1	19.5423	0.9	0.3457
	X2	30.47	1	30.4664	1.41	0.24
	X3	24.88	2	12.4388	0.57	0.5659
	X1*X2	0.86	1	0.863	0.04	0.8424
	X1*X3	119.5	2	59.7498	2.76	0.0711
#	X2 * X3	0	0	0	0	NaN
	Error	1342.07	62	21.6462		
	Total	1594.25	69			





ANOVA results can also be confirmed in Figure 11b, which shows some interesting trends. Figure 11b shows that both motorcycles had a lower mean FE in the first 1000 km, most likely due to powertrain break-in. Then, fuel efficiency was approximately equal for each motorcycle in the intervals between 1k–10k and 10k–15k. However, when the driver changed randomly (<7500 km), both motorcycles showed a tendency towards a higher FE compared to when each one was driven by a single driver (>7500 km). This last result reveals that although the driver had a certain effect on performance (Random FE > Unique FE), the trend of a higher FE for the motorcycle with metal conditioner (A) remained.

In addition, Motorcycle A maintained average FE values higher than Motorcycle B during the whole field test (approximately one km/L), as can be clearly observed in Figure 11b. This represents that Motorcycle A with a 16.1-L fuel tank on average may have an extra 16 km autonomy under the valuated city conditions. This gain of 1 km/L represents around 2.5% of fuel economy improvements (Fuel Economy Improvements, FEI%) with the addition of the metal conditioner.

4. Discussion

The improvement in performance and fuel efficiency of modern engines is mainly related to the optimization of the combustion process, lubrication and contact conditions able to sustain extreme working operation [18]. In this scenario, the engine oil has an important role in reducing friction and wear. Nowadays, the lubricant's ability to meet new specifications and be compatible with older specifications is essential. Therefore, the existence of products that improve fuel economy, reduce friction and wear, that are also compatible with any powertrain and commercial lubricant, as assured by metal conditioner manufacturers, is highly promising [2–4]. However, the use of products not tested by original equipment manufacturing (OEM) leads to insurance loss, and the evaluation of such products is costly and time-consuming [9,12,13,19,24]. This prevents the faster development of lubricating oils since they are restricted in the hands of a few corporations. In order to explore the situation further, one aftermarket additive package, defined as a metal conditioner by its manufacturer, was tested in the laboratory and in the field. The results showed the addition of a metal conditioner provided benefits by reducing friction, wear and fuel consumption. Wear and friction reductions were consistent with the research on the conditioning of cutting tools (enlargement, threading, and drilling) with metal conditioner [14–17].

Tribotests performed in a laboratory presented significant friction and wear reduction when the metal conditioner was added to the 10W-30 engine oil (Figure 3 and Table 6). Although the tribotests were performed with operating conditions and materials that do not mimic engine and gearbox components' material and contact conditions, these results are in agreement with some of the observations from the field analysis. In particular, lower fuel consumption (Figure 11) and lower iron and aluminum wear particles (Table 8) on the motorcycle treated with metal conditioner (Motorcycle A). Nevertheless, it is important to point out that a higher copper content was observed, although below the warning limits presented in the literature [40,42]. Further investigation on wear and tribofilm formation of the transmission kit, piston and cylinder showed irrelevant geometrical variation (<|0.05%|, Table 9), which is in agreement with the oil analysis that indicated a wear content within warning limits (Table 7). These results suggest mild wear and possibly low corrosive wear on the parts made of steel, aluminum and copper. Therefore, in terms of friction and wear, the metal conditioner was shown to improve the overall oil performance.

A major concern of adding aftermarket additives to fully formulated oils is the chemical imbalance it may cause, which can reduce oil performance and service life [1]. In particular, increases in the contents of calcium, zinc, phosphorus and molybdenum additives may increase the frequency of low-speed pre-ignition (LSPI) [11]. As shown by Dohner et al. [24], new motorcycle oil formulation may cause clutch slippage, severe gear wear and other issues that reduce overall performance. In addition, the incorporation of additives into the fully formulated oil might change its performance due to mutual interactions between the additives [9,12,18,23]. The synergistic and competitive effects among additives is a major tribology field of research since the wear resistance provided by lubricants is not always directly correlated with an increase in antiwear additives content or friction reduction [18,19,22,23]. In fact, the presented surface analysis did indicate tribofilm formation with different compositions when MC was added to the engine oil (Figures 6–10), suggesting the MC changes the actuation of the mechanisms of the commercial 10W-30. However, these differences brought some advantages to motorcycle oil friction and wear performance in both laboratory and field studies.

The addition of MC also produced some unexpected changes in oil properties in the small-capacity motorcycles. Figure 4 implies a greater tendency for oil to acidify (TAN) accompanied by a drop in alkaline reserves (TBN) for Motorcycle A. Still, all TAN and TBN values were within the "warning limits" defined by several researchers [12,37–39,41]. It is important to mention that there are no universally accepted warning limits. Different investigators and operating conditions may suggest different limits for a given oil. For instance, in the field study developed by Wolak (2018) [39] with 23 vehicles (capacity of

1332 cc), it was observed that in the first ~4000 km, the maximum increase in TAN was 86%, which is significantly lower than observed in this work for both motorcycles. Macián et al. (2021) [41] stated that the TAN/TBN ratio is particular for each formulation of engine oil, although TBN should always be higher than TAN at the time of the oil drain interval, so the oil formulation ensures a sufficient mileage window. If the TAN value is higher (or close to TBN), the engine oil becomes acidic enough to induce corrosive wear in the lubricated components. Based on the values presented in the literature, the TAN and TBN evolution presented in Figure 4 suggests that both oil formulations (oil and its mixture) had an adequate performance in all the oil change intervals.

Regarding FTIR oil degradation (Figure 5), the analysis must be taken with caution. The standard for FTIR analysis, ASTM D7889 [34], specifies that "6.1 Spectral interferences due to very high levels of external contamination in the fluid can yield errors with these measurements. Common contaminants include the presence of API Group V lubricants at levels exceeding 5% and antifreeze mixes at similar levels". Lubricants of the API V group are mainly polyalkylene glycols (PAG) and various esters. In fact, Macián et al. (2012) [44] also encountered difficulties in detecting FTIR spectral changes associated with fuel contamination in in-service ester-based oil (following the methodology of ASTM D7214 and ASTM E2412). In the present study, the amount of metal conditioner in the mixture (25:1) represents 4% of the mixture, but its formulation, including the base oil, is unknown. In this case, the ASTM E2412 standard suggests that other characteristic bands of degradation products, such as -OH (between 3600–3500 cm⁻¹), must be monitored to confirm if there is actually a substantial level of oil degradation. These recommendations will be considered for future work, since the oil analyses were performed by an outsourced company that only provided the percentage of nitration, oxidation and sulfation advised for API groups I to IV, instead of the FTIR spectra, which should have been required prior to the analyses. Therefore, in relation to this work, it is risky to raise conclusions based on Figure 5, particularly due to the nitration results, which were similar for both motorcycles (Figure 5b) with a tendency to lower values for the oil mixed with metal conditioner, since at these bands there was no interference from MC formulation.

The requirement for better fuel efficiency has led to lower viscosity grades containing friction and viscosity modifier additives in passenger cars [11,37,38]. However, motorcycle oils operate at higher temperatures and also lubricate the clutch and transmission [12,13,24]. Therefore, viscosity reduction might lead to increased operation of the gear set in boundary lubrication, which might lead to severe wear, while the addition of friction modifiers might cause clutch slippage [24]. Thus, different strategies must be used to avoid the premature failure of gears, clutch slippage and excessive oil consumption [13,24]. Although the motorcycle market is growing, such strategies are not as well established as for passenger cars [37,38], but it seems to be a compromise of viscosity reduction and changes in additive packages without compromising gear protection and clutch proper operation [12,13,24]. The results obtained with MC showed slight friction reduction in laboratory tribotests (Figure 3), as well as fuel economy increments (Figure 11) without compromising gear protection (Table 9, Figure 10) and clutch operation. The mechanisms behind the observed performance are unknown but might be related to distinct tribofilm formation and wear reduction, which allow components to perform at optimum conditions [18,22,23]. The average improvement in fuel economy of ~2.5% for both oil drain intervals (1000 km-Regime 0 to 1k, 10k to 15k, and 3000 km-Regime 1k to 10k, Figure 11) is assuredly relevant for Motorcycle A [13,24]. These results suggested fuel economy retention after oil aging along the 15,000 km when the MC was added in the engine oil independently of the oil drain intervals.

In short, the acceptable performance of engine oil in both motorcycles was obtained because there was an adequate balance between viscosity increase, retention of contaminants, acidification (TAN) and additives depletion (TBN). Furthermore, some benefits in terms of reducing friction, wear and fuel consumption were obtained with the addition of a metal conditioner. Thus, the benefits (slight increased wear resistance and fuel economy) provided by, most likely, more reactive AW/EP additives from MC, were greater than their drawbacks (possible yellow metal corrosion).

5. Conclusions

In this work, laboratory and field tests were performed to evaluate the effect of an aftermarket additive. Based on the experimental results, many conclusions were drawn, which are detailed in the following paragraphs.

The powertrain wear results of the steel engine components were consistent with the laboratory studies, in which the tribological performance (friction and wear) was statically improved with the addition of metal conditioner.

The addition of metal conditioner (mixture 25:1) in the motorcycle crankcase and the conditioning of some pieces (80 °C, 90 min) prior to engine assembly brought advantages in terms of the protection of aluminum and iron components during the 15,000 km, which is relevant because aluminum content was found above the warning limits presented in the literature for the motorcycle lubricated with neat SAE 10W-30. However, the addition of metal conditioner increased the wear (ppm/km) of copper metal parts, although at levels below the warning limits.

Physico-chemical properties of the engine oil remained within the acceptable limits across 15,000 km, with or without the addition of metal conditioner. FTIR degradation results demonstrated that certain additives do not allow for a direct comparison between lubricants with and without metal conditioner, as stated by ASTM D7889 and ASTM E2412.

The cylinder, piston, and transmission system pieces showed irrelevant dimension changes (less than 0.05%) in the first 15,000 km of engine operation. However, the lubrication of the transmission kit (crown, pinion, and roller chain) with metal conditioner ensured light wear and longer service life for all its components. Additionally, it significantly increased wear resistance in gear #5.

Fuel consumption in the first 15,000 km of motorcycles was statistically equal (ANOVA, 95% confidence) with or without the application of metal conditioner, for different ranges of oil drain intervals and drivers.

The results indicate that some aftermarket additives can improve lubricants' overall performance without undesired side effects within the lab and field tested conditions. Although promising, this study evaluated only two motorcycles for a short period of time (15,000 km), and further evaluation is required for the results to be considered more representative. Future work also will include analytic and direct ferrography to assess complementary wear particles information.

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References

- Noria Corporation Are Aftermarket Oil Additives Beneficial? Available online: https://www.machinerylubrication.com/Read/ 29610/aftermarket-oil-additives (accessed on 29 May 2022).
- Stewart, C.L. Non-Halogenated Metal Conditioner and Extreme Pressure Lubricant. U.S. Patent US 2004/0,144,952 A1, 29 July 2004.
- Roberts, J. Synthetic Anti-Friction & Extreme Pressure Metal Conditioner Composition and Method of Preparation. U.S. Patent US 2016/0,272,918 A, 22 September 2016.
- 4. Kusch, K. Halogenated Extreme Pressure Lubricant and Metal Conditioner. U.S. Patent 6,028,038, 22 February 2000.
- Miralub Condicionador de Metais-Benefícios. Available online: https://www.miralub.com.br/beneficios.php (accessed on 29 May 2022).
- 6. Militec Brasil Importação e Comércio Ltda Perguntas Frequentes–FAQ–Militec Brasil–Condicionador de Metais. Available online: https://militecbrasil.com.br/perguntas-frequentes/ (accessed on 29 May 2022).
- MotorKote Motorkote 100 Antifricção-Motorkote Brasil. Available online: https://motorkote.com.br/motorkote-100/ (accessed on 29 May 2022).
- NANO Condicionador de Metais FAQ-Condicionar de Metais. Available online: https://www.nanocondicionador.com.br/faq/ (accessed on 29 May 2022).
- Eickworth, J.; Aydin, E.; Dienwiebel, M.; Rühle, T.; Wilke, P.; Umbach, T.R. Synergistic Effects of Antiwear and Friction Modifier Additives. Ind. Lubr. Tribol. 2020, 72, 1019–1025. [CrossRef]
- 10. Stachowiak, G.W.; Batchelor, A.W. Boundary and extreme pressure lubrication. In *Engineering Tribology*, 4th ed.; Butterworth-Heinemann: Waltham, MA, USA, 2014; pp. 371–428.
- 11. Fletcher, K.A.; Dingwell, L.; Yang, K.; Lam, W.Y.; Styer, J.P. Engine Oil Additive Impacts on Low Speed Pre-Ignition. *SAE Int. J. Fuels Lubr.* **2016**, *9*, 612–620. [CrossRef]
- 12. Merry, N.; Mitan, M.; Ramlan, M.S.; Zainul, M.; Nawawi, H.; Kindamas, Z. Preliminary Study on Effect of Oil Additives in Engine Lubricant on Four-Stroke Motorcycle Engine. *Mater. Today Proc.* **2018**, *5*, 21737–21743. [CrossRef]
- Yi Lim, P.; Hui Huang, H.; Richard, K. Additive Technology for Superior and Unique Motorcycle Oil (SUMO). In Proceedings of the JSAE/SAE 2015 Small Engine Technologies Conference & Exhibition, Osaka, Japan, 17–19 November 2015.
- 14. Alves, D.J. Análise Da Viabilidade Técnica e Econômica da Aplicação de Condicionador Metálico em Processo de Alargamento. Master's Dissertação, Universidade Nove de Julho, São Paulo, Brazil, 2014.
- 15. Nunes da Silva, E. Viabilidade Econômica em Processos de Rosqueamento Utilizando Machos de Roscar com Condicionador Metálico. Master's Dissertação, Universidade Nove de Jhulo, São Paulo, Brazil, 2014.
- Santos de Oliveira, F. Avaliação do Desempenho de Machos Tratados com um Condicionador Metálico no Processo de Rosqueamento Interno. Master's Dissertação, Universidade Nove de Julho, São Paulo, Brazil, 2015.
- 17. Coppini, N.L.; Ferreira, S.S.; dos Santos, I.A.; Baptista, E.A.; Costa, E.M. Drilling Analysis of Cemented Carbide Drills after Chemical Treatment under Low Heating. J. Braz. Soc. Mech. Sci. Eng. 2017, 39, 3581–3589. [CrossRef]
- 18. Sgroi, M.; Gili, F.; Mangherini, D.; Lahouij, I.; Dassenoy, F.; Garcia, I.; Odriozola, I.; Kraft, G. Friction Reduction Benefits in Valve-Train System Using IF-MoS2 Added Engine Oil. *Tribol. Trans.* **2015**, *58*, 207–214. [CrossRef]

- Ngo, D.; He, X.; Luo, H.; Qu, J.; Kim, S.H. Competitive Adsorption of Ionic Liquids Versus Friction Modifier and Anti-Wear Additive at Solid/Lubricant Interface-Speciation with Vibrational Sum Frequency Generation Spectroscopy. *Lubricants* 2020, *8*, 98. [CrossRef]
- Cousseau, T.; Ruiz Acero, J.S.; Sinatora, A. Tribological Response of Fresh and Used Engine Oils: The Effect of Surface Texturing, Roughness and Fuel Type. *Tribol. Int.* 2016, 100, 60–69. [CrossRef]
- Siebert, G.; Sinatora, A. Simulation of Piston Ring/Cylinder Bore System Using Tribotests–A Review Focused on the Tribochemical Aspect. In Proceedings of the 25th SAE BRASIL International Congress and Display, Sao Paulo, Brazil, 25–27 October 2016. [CrossRef]
- 22. Huynh, K.K.; Tieu, K.A.; Pham, S.T. Synergistic and Competitive Effects between Zinc Dialkyldithiophosphates and Modern Generation of Additives in Engine Oil. *Lubricants* **2021**, *9*, 35. [CrossRef]
- 23. Lyu, B.; Zhang, L.; Meng, X.; Wang, C. A Boundary Lubrication Model and Experimental Study Considering ZDDP Tribofilms on Reciprocating Friction Pairs. *Tribol. Lett.* **2022**, *70*, 65. [CrossRef]
- 24. Dohner, B.; Michlberger, A.; Castanien, C.; Gajanayake, A.; Hirose, S. Improving Fuel Efficiency of Motorcycle Oils. *Int. J. Fuels Lubr.* 2013, *6*, 1014–1020. [CrossRef]
- Ayerdi, J.J.; Aginagalde, A.; Llavori, I.; Bonse, J.; Spaltmann, D.; Zabala, A. Ball-on-Flat Linear Reciprocating Tests: Critical Assessment of Wear Volume Determination Methods and Suggested Improvements for ASTM D7755 Standard. *Wear* 2021, 470–471, 203620. [CrossRef]
- 26. Seabra, J.H.O. Mecânica Do Contacto Hertziano, 2nd ed.; Faculdade de Engenharia da Universidade do Porto: Porto, Portugal, 2003.
- 27. Cousseau, T.; Serbino, E.; Rejowski, E.; Sinatora, A. Influence of Steadite on the Tribological Behavior of Cylinder Liners. *Ind. Lubr. Tribol.* **2018**, *71*, 324–332. [CrossRef]
- ASTM D445-21; Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (the Calculation of Dynamic Viscosity). ASTM International: West Conshohocken, PA, USA, 2021; Volume 5.01. [CrossRef]
- ASTM D4739-17; Standard Test Method for Efficient Basicity Determination by Potentiometric Hydrochloric Acid Tritation. 2017. ASTM International: West Conshohocken, PA, USA, 2018; Volume 5.02. [CrossRef]
- ASTM D974-21; Standard Test Method for Acid and Base Number by Color-Indicator Titration 1. Annual Book of ASTM Standards. ASTM International: West Conshohocken, PA, USA, 2018; Volume 5.01. [CrossRef]
- 31. *ASTM D2270-10;* Standard Practice for Calculating Viscosity Index from Kinematic Viscosity at 40 °C and 100 °C. ASTM International: West Conshohocken, PA, USA, 2016; Volume 5.01. [CrossRef]
- 32. *ASTM D7899-19;* Standard Test Method for Measuring the Merit of Dispersancy of In-Service Engine Oils with Blotter Spot Method. ASTM International: West Conshohocken, PA, USA, 2020; Volume 5.04. [CrossRef]
- ASTM D91-02; Standard Test Method for Precipitation Number of Lubricating Oils. ASTM International: West Conshohocken, PA, USA, 2019; Volume 5.01. [CrossRef]
- ASTM D7889-21; Standard Test Method for Field Determination of In-Service Fluid Properties Using IR Spectroscopy. ASTM International: West Conshohocken, PA, USA, 2021; Volume 5.04. [CrossRef]
- ASTM D5185; Standard Test Method for Multielement Determination of Used and Unused Lubricating Oils and Base Oils by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). ASTM International: West Conshohocken, PA, USA, 2018; Volume 5.02. [CrossRef]
- ASTM D7684-11R20; Standard Guide for Microscopic Characterization of Particles from In-Service. ASTM International: West Conshohocken, PA, USA, 2020; Volume 5.04. [CrossRef]
- 37. Wei, L.; Duan, H.; Jin, Y.; Jia, D.; Cheng, B.; Liu, J.; Li, J. Motor Oil Degradation during Urban Cycle Road Tests. *Friction* **2021**, *9*, 1002–1011. [CrossRef]
- Agocs, A.; Lajos Nagy, A.; Tabakov, Z.; Perger, J.; Rohde-Brandenburger, J.; Schandl, M.; Besser, C.; Dörr, N. Comprehensive Assessment of Oil Degradation Patterns in Petrol and Diesel Engines Observed in a Field Test with Passenger Cars-Conventional Oil Analysis and Fuel Dilution. *Tribol. Int.* 2021, 161, 107079. [CrossRef]
- Wolak, A. Changes in Lubricant Properties of Used Synthetic Oils Based on the Total Acid Number. *Meas. Control.* 2018, 51, 65–72. [CrossRef]
- 40. Booser, E.R. Handbook of Lubrication and Tribology. In *Monitoring, Materials, Synthetic Lubricants, and Applications,* 1st ed.; Booser, E.R., Ed.; CRC Press: Boca Raton, FL, USA, 1993; Volume III; ISBN 9780367802493.
- Macián, V.; Tormos, B.; García-Barberá, A.; Tsolakis, A. Applying Chemometric Procedures for Correlation the FTIR Spectroscopy with the New Thermometric Evaluation of Total Acid Number and Total Basic Number in Engine Oils. *Chemom. Intell. Lab. Syst.* 2021, 208, 104215. [CrossRef]
- 42. Eurofins TestOil Resource Guide, Monitoring & Alarming Wear Metals. Available online: http://forms.testoil.com/acton/media/ 4748/oil-analysis-monitoring-and-alarming-wear-metals (accessed on 28 April 2022).
- 43. ASTM E2412-10; Standard Practice for Condition Monitoring of Used Lubricants by Trend Analysis Using Fourier Transform Infrared (FT-IR) Spectrometry. ASTM International: West Conshohocken, PA, USA, 2018; Volume 5.05. [CrossRef]
- 44. Macián, V.; Tormos, B.; Gómez, Y.A.; Salavert, J.M. Proposal of an FTIR Methodology to Monitor Oxidation Level in Used Engine Oils: Effects of Thermal Degradation and Fuel Dilution. *Tribol. Trans.* **2012**, *55*, 872–882. [CrossRef]
- Eisentraut, K.J.; Newman, R.W.; Saba, C.S.; Kauffman, R.E.; Rhine, W.E. Spectrometric Oil Analysis: Detecting Engine Failures before They Occur. Anal. Chem. 1984, 56, 1086A–1094A. [CrossRef]

- 46. Papadopoulos, P.; Priest, M.; Rainforth, W.M. Investigation of Fundamental Wear Mechanisms at the Piston Ring and Cylinder Wall Interface in Internal Combustion Engines. *Proc. Inst. Mech. Eng. Part J J. Eng. Tribol* **2007**, 221, 333–343. [CrossRef]
- 47. Çavdar, B.; Ludema, K.C. Dynamics of Dual Film Formation in Boundary Lubrication of Steels Part I. Functional Nature and Mechanical Properties. *Wear* **1991**, *148*, 305–327. [CrossRef]