

CHANGES IN FUNCTIONAL PROPERTIES OF ENGINE OILS DURING EXPLOITATION – TBN

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Abstract: The article presents the analysis of functional properties of engine oils during operation based on TBN (Total Base Number). The results obtained with the application of the traditional, accredited research method have been compared with the results of the study conducted with the use of a modern tool (FluidScan) which allows to determine the TBN value in less than a minute. Three types of engine oils have been analyzed and each of them was given a separate letter code: CE, MS and PE. The oils have been compared during the entire exploitation process from the first application until the oil change [mileage: 11 300 km (δ (standard deviation)=2580km)].

Keywords: engine oil, lubricants, TBN, FluidScan, exploitation

1. INTRODUCTION

According to current knowledge, the quality of engine oil may be determined based on several tests, from the assessment of physical and chemical properties in laboratories to the evaluation of the properties after long-term and particularly expensive exploitation research [Alistair 2005, Caneca *et al.* 2006, Adams, Romeo and Rawson 2007, Litwiński and Piec 2007, Robinson 2007, Latif and Dickert 2011, Bessser *et al.* 2012, Bassbasi *et al.* 2013, Braga, dos Santos and Martin 2014]. Knowing and understanding the characteristics of engine oils, as well as developing effective methods of analysis enables the creation of quality monitoring systems that could be conducted during the entire life-cycle of the engine. In their study,

W. Urzędowska and Z. Stępień, point out that in order to ensure a fully safe and reliable operation of the engine it is necessary to monitor multi-directional changes in engine oil properties during its use, which of course entails the introduction of adequate norms and procedures [Urzędowska and Stępień 2008, 2012a, 2012b] While selecting the physical and chemical properties of the engine oils which were to be monitored in order to evaluate the degradation level, the changes in washing and dispersing potential of the oil were considered and assessed based on the decline of the Total Base Number.

To analyze the above mentioned changes in TBN, the potentiometric titration method was applied to the glass and reference electrodes. The equivalence point was set on the potentiometer reading for the buffer solution at a specific potential expressed in mV. The results have also been obtained with the use of a portable infrared spectrometer (FluidScan[®] Apparatus).

2. RESEARCH MATERIAL

Lubricating engine oils that complied with the internal specifications of Mitsubishi Company were admitted to the research. Mitsubishi was also the producer of the engines in the study. The research material consisted of engine oils coded as CE, MS and PE. The quality of the engine oils was assessed in the same types of cars and during the same period of time. The cars that took part in the research were similar in terms of their make, type and exploitation conditions. They all came from the fleet of Małopolska Training Center for Drivers (MORD). The total number of nine vehicles with the cylinder capacity of 1332 cm³ with petrol engines and operating on the same batch of fuel were used in the research. Figure 1 and table 1 show

the MORD's car fleet together with a full specification of the selected car model. All cars were used for driver license exams. Each of the oils was applied in three cars. At first, the freshly applied oil was tested and then the test was repeated every quarter of the year in the course of a twelve-month. After the first, then the second, third and fourth quarter of the year, the total number of nine samples from each oil type was collected, which makes 36 samples within a year.



Figure 1. Mitsubishi Colt Z30 cars which were selected to the research. Source: Authors' own work, based on mord.pl and P.U.H. Auto-Complex Zdzisław Czerwiński

Table 2 shows the engine oils which were selected to the research – class SAE 5w/30, together with the requirements of API, ACEA classifications and engine producers.

Table 1. Mitsubishi Colt Z30 cars specification, which were selected to the research.

Item			Z30
			XNLHL6/XNLHR6
Vehicle dimension [mm]	Front track	1	1.460
	Overall width	2	1.695
	Front overhang	3	845
	Wheel base	4	2.500
	Rear overhang	5	595
	Overall length	6	3.940
	Ground clearance (unladen)	7	154
	Overall height (unladen)	8	1.550
	Rear track	9	1.445
Vehicle weight [kg]	Kerb weight	Without optional parts	970
		With optional parts	1.038
	Max. gross vehicle weight		1.460
	Max. axle weight rating-front		745
	Max. axle weight rating-rear		745
	Towing capacity	With brake	1000
		Without brake	500
	Max. trailer-nose weight		50
Seating capacity			5

Engine	Model code	4A90
	Type	DOHC MIVEC
	Total displacement [ml]	1.332
	Maximum output [kW/rpm]	80/6.000
	Maximum torque [N-m/rpm]	145/4.000
Fuel system	Fuel supply system	MPI
Transmission	Model code	F5MGA
	Type	5-speed manual transmission
Turning radius [m]	Body	5.4
	Wheel	5.1

Source: Authors' own work, based on mord.pl and P.U.H. Auto-Complex Zdzisław Czerwiński

Table 2. Quality and viscosity classifications of the engine oils selected to the research

OIL	SAE	ACEA	API	Classification by engine manufacturers
CE	5w-30	A3, C3	SH	VW 504 00; BMW Longlife-04; MB-Approval; 229.31/ 229.51; Porsche C30
MS	5w-30	C3	SM/SL	General Motors Service Fill dexos2™ (license number GB1A0914015); BMW Longlife 04; MB 229.31/229.51; Volkswagen (benzyna) 502 00 / 505 00
PE	5w-30	C2	-	JASO - DL-1

Source: Authors' own work

The additional information provided by the manufacturers shows that:

- 1) Oil with the code CE has a durability of VW.
- 2) Oil with the code MS complies with the latest specifications for engine oils stipulated by major car manufacturers and is compatible with most pollution filters designed for Diesel engines, as well as all catalytic convertors for gasoline engines. It offers excellent performance at both very high and very low operating temperature and extends engine protection against wear, deposits and sludge formation. Oil with the code MS is especially recommended for use in the following brands of vehicles: Mercedes-Benz (which requires MB 229.31 or 229.51), BMW (which requires Longlife Oil 04), Volkswagen (which requires VW 502 00 / 505 00). This oil is also approved by General Motors Service Fill dexos 2 TM, which is required in all latest models of 2010 GM/Opel/Vauxhall/Chevrolet cars with Diesel or gasoline engines. GM/Opel manufacturers recommend the dexos2TM specifications as compatible with the older GM/Opel ones (GM-LL-A-025 and GM-B-LL-025). The oils which meet the requirements of dexos2TM can also be used in most cars manufactured by GM/Opel/Vauxhall/Chevrolet with Diesel or gasoline engines.
- 3) Oil with the code PE is a product created specifically for the Japanese brands of cars. It is recommended for engines with spark or compression ignition, with turbo charging or without it, of the following car brands: Mazda, Toyota, Suzuki, Nissan and Mitsubishi. It works very well both in city traffic and on highways. The oil is compatible with exhaust gas treatment devices such as: DPF and TWC. It guarantees reliable engine operation in the summer and winter. It is also recommended for vehicles that meet Euro 5 emission standards.

When analyzing changes in the properties of engine oils, it should be kept in mind that the vehicle operating conditions were “difficult”. By that the actual conditions are meant, which in the case of this particular study were:

- car operation requiring a large and variable engine load (alternating between rapid;
- overheating and cooling of the engine);
- extended periods of engine operation on idle mode (due to traffic congestion);
- short distance driving (multiple warming and cooling of the engine);
- frequent engine starting at low temperatures;
- driving in traffic jams (driving conditions referred to as “drive-stop”).

Table 3 presents details concerning the number of kilometres travelled by each car considered in the study.

Table 3. The number of kilometres travelled by each car. Source: Authors’ own work

The sample code	Mileage at start [km]	Mileage after 1 st quarter [km]	The number of kilometres [km]	Mileage after 2 nd quarter [km]	The number of kilometres [km]	Mileage after 3 rd quarter [km]	The number of kilometres [km]	Mileage after 4 th quarter [km]	The number of kilometres [km]
CE 17760	12858	17259	4401	20789	7931	24216	11358	26078	13220
CE 17977	6033	9006	2973	11673	5640	14829	8796	16008	9975
CE 18716	9477	12557	3080	15837	6360	19486	10009	21646	12169
MS 18011	13486	15691	2205	18685	5199	20751	7265	22491	9005
MS 18128	14571	16379	1808	19789	5218	23344	8773	25374	10803
MS 18793	6223	7041	818	7343	1120	9463	3240	12323	6100
PE 17939	12370	16550	4180	21176	8806	24360	11990	25436	13066
PE 18024	11694	15452	3758	17575	5881	21897	10203	23442	11748
PE18689	13290	17234	3944	22039	8749	27264	13974	28821	15531

3. RESEARCH METHODOLOGY

In recent years, more and more procedures of monitoring the engine oil properties during operation have been developed and introduced [Alistar *et al.* 1996, Agoston, Ötsch and Jakoby 2005, Trojan and Krasodomski 2005, Urzędowska and Stępień 2008, Al-Ghouti, Al-Degs and Amer 2010, Felkel *et al.* 2010, Geach 2015]. This has been done to ensure all required functional and operational properties of the engine oils through the verification of oil change intervals which, of course, depend on the operating conditions associated with quantitative and qualitative processes of engine lubricant degradation [Ziba-Palus and Kościelniak 1999, Podniało 2002, Jakóbiec and Budzik 2007, Jakóbiec 2008, Litwiński 2011, Podniało 2012, Kral *et al.* 2014, Urzędowska i Stępień 2012a-c]. This study focuses on the assessment of changes in physical and chemical properties of engine oils based on the changes in their washing and dispersing potential.

Engine oils may contain weak bases which are quantified through the so called Total Base Number (TBN) or alkaline reserve. It is defined as the number of milligrams of potassium hydroxide (KOH) equivalent to all base components contained in 1 g of the test product [PN-76-C-0416 1976]. The determination was based on titration of a solution of a weighted amount of test substance in a solvent containing the indicator [PN-98-C-04049 1998]. A solution containing toluene, isopropyl alcohol and water was used as a solvent. The titration was performed with standard hydrochloric acid solution (HCL) - potentiometrically and against indicators [PN-81-C-04530.00 1981]. The samples taken in the first quarter of the study were marked by titration against indicators; however, with an increase of kilometers traveled, the color of engine oils made the further use of this method impossible. The potentiometric titration was then introduced [Robinson 2007].

The alkaline reserve was also measured with the use of FluidScan[®] (fig. 2) and thus obtained results provided a good comparison with the other method.



Figure 2. FluidScan[®]. Source: Authors' own work

FluidScan[®] is a tool which enables very fast measurements of the following parameters:

- 1) the degree of oxidation, nitration and sulfonation (ASTM D7412 (FTIR);
- 2) glycol (ASTM D7624(FTIR);
- 3) soot (ASTM D5967);
- 4) TBN (ASTM D4739);
- 5) TAN (Total Acid Number)(ASTM D664);
- 6) water (ASTM D6304).

3.1. FluidScan[®] - a portable infrared spectrometer

FluidScan[®] is a portable infrared spectrometer which enables the assessment of operational properties of fluids in accordance with international standards (ASTM); it is fitted with sophisticated oil analysis software (JOAP). It provides a quick access to information which can be used to assess the performance and operational properties of the given fluid.

Thanks to the application of a patented measuring cuvette filled from the top, FluidScan® does not require any prior preparation of the sample or time-consuming cleaning of the measuring system. Such a solution facilitates the analysis of oil exactly where the machines are used.

The ‘heart’ of FluidScan® is its innovative spectrometer working in the mid-infrared range. The spectrometer receives the infrared radiation passing through the oil sample in the measuring cuvette using waveguide. Then, the waveguide carries the radiation onto the prism – a diffraction grating which directs it to the advanced detector recording the image spectrum of the sample. This approach maximizes the amount of radiation that reaches the spectrometer, which in turn increases the optical performance and spectral resolution. Physically, the measurement has the following phases: the introduction of the sample from the top of the measuring system, the approval of the information about the sample, and the analysis performed with the use of an intuitive interface. In a matter of seconds the sample status is visible on the screen together with the parameter measure results, which are saved in the machine’s memory. FluidScan® Manager software enables data transfer to the software installed on the computer. This software allows data logging, trending and it also sends an alert in case of an occurrence of potential failure. FluidScan® does not require computers to perform analyses; however, FluidScan® Manager facilitates the collection and processing of the data obtained. The results of measurements stored in the database can be synchronized with the FluidScan® Manager software thus allowing to generate full diagnostic reports of investigated fluids. The results obtained during the measuring process help determine the level of degradation of the lubricant and the extent of its pollution with other fluids (water, glycol, unsuitable oil) exactly where the machine operates. FluidScan®

also enables the measurement of key performance characteristics of lubricants and synthetic or petroleum fluids.

The small size of the spectrometer allows those working on diagnosed vehicles (trucks, wind turbines, military equipment etc.) to implement the program of “predictive use” based on the investigated properties of lubricants.

The main advantages of conducting oil analyses “to date” and “on the spot” (where the machines operate) are:

- extending the period between oil checks;
- no need to wait for the results of laboratory tests/analyses;
- reduced equipment maintenance and operational costs;
- prevention of unplanned maintenance activities;
- prevention of serious accidents.

Another important feature of this analytical tool is that it was designed with the use of modern technology with the aim to reduce electricity consumption. That is why it is not only a reliable and durable piece of equipment, but it can work up to eight hours because it is powered by lithium-ion batteries.

The designers and constructors have come up with a product which is user-friendly, easy to use, allows to make an entire series of measurements according to a specifically set and programmed order, and finally reading or transmission of measurement results after the completion of the test on site (where the machines operate).

4. RESEARCH RESULTS (PRESENTATION AND ANALYSIS)

Changes in washing and dispersing potential of the oil, assessed on the basis of the decline in the Total Base Number had a 'parabolic' course and were relatively big. The most intensive changes were observed in the range (0 – 8000) km. In all oil groups the degradation process proceeded with the greatest speed until $\frac{1}{2}$ of the exploitation time, after that the changes continued at a slower pace, thus the graph that could be obtained based on the results would have a shape of exponential curve. Engine oils with the code MS showed the smallest depletion of detergent-dispersive potential and an increase in destructive products. While making final conclusions of this study, the differences in mileage of the investigated vehicles were of course taken into consideration. As a result of the use of the engine oil with the code PE, a particularly high level of dispersed soot was observed, which led to a decrease in effectiveness of detergent-dispersive additives. The EP oil start level, which was 4.2 mg KOH/g, was the lowest among the three analyzed oil groups. In all three cases, the common denominator of the oil groups was their rapid loss of the alkaline reserve that is the ability of the lubricant to neutralize acidic combustion products which manifests itself in a faster decrease in the Total Base Number after the first thousand kilometres travelled. The largest percentage decrease in the Total Base Number relative to the initial value after only two quarters of research was observed in the PE 017939 oil (a decline by 62%, mileage 8 806 km). At 12 000 km traveled, the largest percentage decrease was observed in the CE 017977 oil (from 0.6 to 1.8 mg KOH/g). It is worth mentioning here that such a rapid degradation of the detergent-dispersive additives is the basis for shortening (up to a half) the time intervals between oil engine changes.

In conclusion, it should be noted that all of the above was based on the results of research conducted with the use of approved and accredited test methods. The results obtained with the FluidScan® equipment are discussed below.

Table 4. Changes in Total Base Number [mg KOH/g]. Source: Authors' own work

	<u>Oil</u>	<u>The sample code</u>	<u>Method</u>	<u>Changes in Total Base Number [mg KOH/g]</u>				
				<u>Fresh oil</u>	<u>After 1st quarter</u>	<u>After 2nd quarter</u>	<u>After 3rd quarter</u>	<u>After 4th quarter</u>
Car brand - Mitsubishi Colt Z30 (1332cm3)	CE	CE 017760	INiG	6.00	4.85	2.91	2.13	2.43
			FluidScan	7.10	4.70	1.20	0.00	0.00
		CE 017977	INiG	6.00	5.30	3.40	1.75	2.03
			FluidScan	7.10	5.70	4.20	3.00	2.70
		CE 018716	INiG	6.00	5.50	3.32	1.90	2.15
			FluidScan	7.10	3.90	2.40	0.80	0.90
	MS	MS 018011	INiG	6.18	6.70	3.63	3.12	3.16
			FluidScan	6.40	3.70	1.60	0.70	0.00
		MS 018128	INiG	6.18	6.50	3.57	3.22	3.23
			FluidScan	6.20	3.90	1.60	0.00	0.00
		MS 018793	INiG	6.18	7.20	6.35	5.44	5.17
			FluidScan	6.40	5.90	5.70	5.90	2.50
PE	PE 017939	INiG	4.17	3.90	1.60	1.64	1.59	
		FluidScan	6.30	3.20	1.70	1.10	1.20	
	PE 018024	INiG	4.17	4.38	1.64	1.55	1.45	
		FluidScan	6.30	4.20	1.40	1.50	0.70	
	PE 018689	INiG	4.17	4.05	1.62	1.33	1.29	
		FluidScan	6.30	4.00	2.00	0.20	0.10	
		<u>Correlation coefficient</u>	<u>0.53</u>	<u>0.39</u>	<u>0.76</u>	<u>0.66</u>	<u>0.31</u>	

The final stage of the research was an attempt to determine the relationship between the results obtained by different methods (the officially accredited one and the portable FluidScan[®] device). Pearson's correlation coefficient was used. On analyzing the individual correlation coefficients, it was found that the maximum correlation exists in relation to the measurement of engine oil after the second and third quarter. After these two periods, the correlation between the results was positive, and its force was at a high level (from 0.66 to 0.76). The average correlation of 0.39 and 0.31 was obtained on comparing the results of these two methods with regard to the oil samples tested after the first and fourth quarter. This means that the results obtained by these two methods are in fact similar to each other and can be used interchangeably. However, looking at individual records in more detail, it appears that in some cases the results obtained are completely different. In case of the fresh oil, the results are relatively similar in the MS oil, then for CE oil and finally for PE oil. After the first quarter, almost identical results were obtained for samples CE 017760 and all samples from the PE group. The greatest differences were observed in case of the samples MS 018011 (45%) and MS 018128 (40%). After the second quarter, the situation looks very similar to the previous measurement period i.e. the most similar results are obtained in all samples from the PE group, the sample MS 018793, and CE 017977. After the third quarter, only three out of ten results are connected. This also refers to the samples: PE 017939, PE 018024 and MS 018793. It should be noted that the mileage of the first two samples is 11 990 and 10 203 km respectively. Compared with other samples, such mileage is relatively high. The situation after the last measurement period is analogical. The most correlated with each other are the results obtained for the oil samples PE 017939, PE 018024. Additionally, the results for the oil sample CE 017977 deserve further notice.

For the remaining samples, the results obtained with the FluidScan[®] significantly differ from those obtained through accredited methods.

5. CONCLUSIONS

Based on the results obtained it was found that:

- The TBN results obtained by different methods are consistent to varying degrees. Depending on the degree of degradation of engine oil, the FluidScan[®] can be used to determine changes in washing and dispersing potential of the oil. This might be of particular value for the car fleet owners, who may wish to analyze and monitor the properties of engine oils in their cars themselves. However, in order to make use of the latest innovations and benefit from them, it is necessary to invest quite a lot in new tools and equipment. This is a barrier which prevents individual car users from being able to benefit from the latest methods and innovations. As W. Urzędowska and Z. Stępień rightly put it – in order to determine the best time of oil change, individual car users have to rely on their ‘hunch’ [Urzędowska and Stępień 2012b].
- In most laboratories, the analyses of operational properties of lubricants are performed with the use of titration methods. The results of this study give an optimistic forecast for the future when it comes to the development and improvement of well-known, conventional laboratory equipment. Not only time but also money will be saved since the reagents which are now still needed to perform different analyses and are quite expensive might not be used so often anymore (it is particularly noticeable in case of TBN tests). The device used

in this study is also environmentally friendly, which is particularly important nowadays when selecting research methods.

- The advantage of FluidScan[®] is its ability to obtain reliable results of the following parameters: the degree of nitration and sulfonation, Total Acidity Number, the content of water, glycol and soot. FluidScan[®] also classifies operational fluids by type, taking into account their chemical composition, application and the image in infrared spectrum. The spectrum of each type of the fluid varies depending on the degree of contamination and degradation. Using appropriate algorithms, it is possible to determine, quite accurately, the degree of such degradation which is exactly what the FluidScan[®] does, and that is why it is a very useful tool in the process of monitoring and maintenance of the equipment through oil analyses.
- There is a need for further studies in relation to the contamination in oil (water) – with the use of comparative methods. In their studies, W. Urzędowska and Z. Stępień point out that FTIR does not allow to fully detect many of the contaminants in oil (e.g. water). Perhaps, this might be changed with the use of FluidScan[®].
- The continuous development and introduction of new test methods related to engine oils is absolutely essential and it should be adjusted to the changes in quality of the latest products as well as their operating conditions.
- The alkaline reserve is of great importance for the assessment of operational properties of engine oils, especially the oil samples taken during the operation (used oil), in order to determine the future

performance. The higher the value of alkaline reserve, the later are the acidic products of wear are visible in oil.

The Total Base Number is a parameter characteristic for engine oils with base/alkaline additives e.g. engine oils with alkaline reserve. Such additives play an important role in neutralizing the acids formed during combustion of engine fuels containing sulphur and dispersing particles of soot. During combustion, sulphur changes into sulphur dioxide which together with water forms aggressive sulphur acids. Alkaline additives in engine oils neutralize these acids.

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STRESZCZENIE

Artykuł zawiera analizę właściwości użytkowych olejów silnikowych w warunkach eksploatacji w oparciu o zmianę liczby zasadowej (TBN). Wyniki uzyskane dzięki tradycyjnej, akredytowanej metodzie porównano z wynikami uzyskanymi dzięki nowoczesnej aparaturze (Fluidscan[®]), który wartość TBN, umożliwia określić w czasie kilkudziesięciu sekund. W warunkach eksploatacyjnych analizie poddanych zostało trzy oleje silnikowe zakodowane, jako: CE, MS oraz PE. Porównanie wybranych olejów obejmowało cały zakres eksploatacji, to znaczy od momentu zalania olejem silnika do momentu wymiany oleju [przebieg 11 300 km ($\delta = 2580$ km)].

Słowa kluczowe: olej silnikowy, smar, TBN, FluidScan[®]