

Robert Mamgbi

Department of Organic Technology and Refinery Processes, Faculty of Chemical Engineering and Technology, Cracow University of Technology, Cracow

Jaroslav Cerny

Department of Petroleum Technology and Alternative Fuels, Faculty of Environmental Protection, Institute of Chemical Technology in Prague, Czech Republic

Erasmus Barifaijo

Makerere University, Department of Geology and Petroleum Studies, Kampala, Uganda

Time of Exploitation and Detergency Properties of Low SAPS Engine Oil

Modern Generations of Low SAPS (Sulphated Ash, Phosphorus, Sulphur)

Enforcing the EURO IV limit was brought about due to the need to protect the environment and smartly clean exhaust gases. Actually in gasoline engine it is particularly solved by using three way catalysts. In diesel engines to reduce the concentration of oxides of nitrogen and solid particles in the exhaust emission is more difficult. So for this reason, systems like EGR (*Exhaust Gas Recirculation*) recycles some of the flue gas back to the engine, thus reducing the amount of harmful substances in the exhaust emission. The second one is the selective catalytic reactor that effectively removes oxides of nitrogen by reducing it with urea to inert nitrogen gas. For the solid particles, diesel particle filters (DPF) were used to catch and retain the particles in the exhaust tract [4, 10, 17].

In the last decade the environmental regulations have been significantly affected in the automotive industry. Since 2005 the maximal sulphur content in fuels has been 50 ppm but regional 10 ppm fuels have to be available in the EU by then. Now the regulations are even stronger and the level of sulphur content in diesel fuel is only 5 ppm. New emission standards and resulting engine design changes, lead to changes also in performance effectiveness of lubricants. Nowadays the Euro V and yet to come Euro VI standards are leading to one of the most significant changes in lubricant quality since the start of Euro emission targets.

The challenge for the lubricants industry is to provide engine oils with both extended drain intervals and fuel economy while also formulating after treatment compatible engine oils. Organic compounds of calcium or magnesium are used as effective detergents and reducing their content may change the detergent properties of the oil.

Since the introduction of auto catalysts in the 1970s, the effects of sulphated ash, phosphorous and sulphur (SAPS) in engine oils on catalyst performance and durability have been continuously monitored. However the deterioration and emission attributed to the oil was difficult to quantify. Sulphated ash in the oil is derived from the salts of alkaline earth metals and detergent additives. These additives help to keep the engine surface free of combustion deposits because of the ZnDDP (Zinc dialkyldithiophosphate) anti-wear and antioxidant agents in the oil [5].

Many studies have been published examining the effect on gasoline catalyst activity of phosphorus level from (ZnDDP) and detergent components that contains calcium in the engine oil, but there are less published works on diesel catalyst. If compounds such as zinc phosphates from (ZnDDP) are deposited on a catalyst they can form a diffusion barrier preventing exhaust gas molecules reaching the active sites. The studies were often performed with bench engines and extended ageing was simulated. This

was done by passing oil through the engine in a short time period (for example, 100 hours) equivalent to the amount which would have been consumed in 80.000 km of road driving (ageing) by a vehicle. The fuel was doped with lubricating oil and the mixture combusted in the engine. In some cases the engine inlet valve seals were removed to increase oil consumption. The studies generally showed that phosphorus reduced catalyst activity and that increased phosphorus levels enhanced deactivation. However, increasing the ratio of alkaline earth metal to phosphorus decreased the quantity of phosphorus deposited on the catalyst [5].

Concerns have been expressed that such studies do not simulate real world deactivation because of the accelerated oil consumption, operation at fixed engine speed/load conditions and non-representative means of oil consumption. However, there are further aspects that influence vehicle fleet studies, such as thermal deactivation, shifts in oxygen response characteristics and other engine calibration factors over time, as well as differences in the levels of phosphorus deposition on the catalyst. A few vehicle trial results have been published and all conclude that although

the vehicles have invariably met the emission limits for which they were designed, the non-destructive removal of phosphorus noticeably improves catalyst performance, especially light-off.

With severer emission limits under discussion, together with extended durability requirements, the impact of SAPS on catalysts and filters is increasing the need to develop low SAPS oils that do not compromise engine wear or oil consumption. The oil additives industry is actively focusing on this, and may ultimately require the availability of ashless, phosphorus- and/or sulfur-free components and the use of higher quality, low-sulfur base stocks, all of which adds complexity and cost to the formulations [5].

With new rules on emission limits and new engine design especially in the EU, some researchers argued that reducing the amount of SAPS might not be the way forward especially when it comes to additives and engine safety. Reducing SAPS level constrains formulation options, presents a risk to engine integrity and may close out desirable additive and base oil options [5].

Lubricants are now under tight watch, a wide range of after treatment options are emerging and each option

Table 1. Overview of the catalyst and the negative effect on the filter used

Equipments		Negative effects of the critical elements		
		Ash	Phosphorus	Sulphur
Filter for Solid Particulate	DPF	yes	-	-
Continual Regeneration Trap	CRT	yes	-	-
Three Way Catalyst	TWC	-	yes	-
Diesel Oxidation Catalyst	DOC	-	yes	yes
Lean NO _x Catalyst	LNC	-	-	yes
NO _x Absorber	NO _x	-	-	yes
Selective Catalyst Reduction	SCR	-	?	?

Table 2. Limits of the critical elements of Phosphorus, Sulphur and Ash in the new generations of motor oil

Classifications	Current motor oil		New generation motor oil
API	Phosphorus	API SH max. 0.12%	Phosphorus API SM 0.06±0.08%
		API SJ, SL max. 0.10%	
	Sulphur: not determines	Ash: not determined	Sulphur: max. 0.2%
ACEA small engines	Phosphorus: not determined		Phosphorus: max. 0.5% (C1), 0.8% (C2, C3)
	Sulphur: not determines		Sulphur: max. 0.2% (C1), 0.3% (C2, C3)
	Ash: max. 1.6%		Ash: max. 0.5% (C1), 0.8% (C2, C3)
ACEA big engines	Phosphorus: not determined		Phosphorus: max. 1.0%
	Sulphur: not determined		Sulphur: max. 0.3%
	Ash: max. 2.0%		Ash: max. 0.8%

has its own potential sensitivity to lubricant components. Evidence linking deterioration in A/T system performance to lubricant composition is weak. Need for change to lubricant formulation is not strongly justified and there is a risk that engines will suffer deterioration in wear and cleanliness performance [4, 10, 17].

Formulation of a new generation of motor oil are to work effectively with engines that contains sensitive filters and catalyst, that is why these new generations of motor oil have very low levels of sulphated ash, low amounts of

phosphorus, and sulfur which are poisonous to the catalysts and shortens the effectiveness and lifecycle of these equipments [4, 10, 17].

Government clean – air act legislation is forcing technological changes in the low SAPS technology to produce new generation engine oils that support the most technically advanced engine operations and emission performances in the automotive industry, they are an example of how technology improves the performance and extend the lifespan of machinery.

Experimental methods used

Samples of oil used

The used oils were of the Shell Helix VX VW 504.00/507.00 (VX 5W-30) specification for the main experiment and only some additional motor oils of the ACEA A3/B4 (Mogul GX SEA 15W-40) specification

and VW 504.00/507.01 (Texaco Havoline ultra V SAE 5W-30) which were collected at a lower drained interval from 7600÷15.000 km were used for the blotter spot test as a comparative standard.

Samples of the used oils were obtained from the Jarov auto service in Prague, Czech Republic, and taken from

Table 3. Type of cars, engine specification, tachometer, distance travelled and oil used during the flexible extended service interval

Samples	Cars	Engine	Oil used		Tachometer	Distance travelled
1	Sharan	TDI 1,9 AUJ	Oil 1 Diesel Engines		89.490	14.383
2	Audi	TDI 2,0 BLB			47.454	21.000
3	Audi A4	TDI 2,5 AKE			182.276	21.000
4	Audi	TDI 2,5 BAU			101.134	25.000
5	Audi	TDI 2,5 BAU			82.696	25.696
6	Porsche	Diesel			-	26.258
7	Octavia II	TDI 2,0 BKD			27.075	27.075
8	Octavia II	TDI 1,9 BJB			134.002	28.907
9	Superb	TDI 2,5 BGD			49.492	29.036
10	Caddy	TDI 1,9 BLS			58.951	29.491
11	Transporter	TDI 1,9 AXC			57.961	29.828
12	Passat	TDI 2,0 BKP			59.312	30.262
13	Octavia II	TDI 1,9 BKC			93.510	31.152
14	Transporter	TDI 1,9 AXB			276.251	31.563
15	Fabia	1,2 HTP	Oil 1 Gasoline Engines		121.309	16.016
16	Golf	1,6 BCB			84.020	26.000
17	Octavia II	1,8 T			64.403	29.802
18	Fabia	1,2 HTP			64.511	30.320
19	Golf	1,6 BGU			62.772	33.719
20	Golf	1,9 TDI	Oil 2	Only for blotter spot test, comparative standard	256.098	7.600
21	Golf	1,9 TDI			264.330	15.000
22	Fabia	1,2 HTP	Oil 3		117.683	15.000
23	Octavia II	1,9 TDI			108.448	15.000

Oil I... Shell Helix VX VW 504.00/507.00 (5W-30), Oil II... ACEA A3/B3 (Mogul GX SAE 15W-40), Oil III... Texaco Havoline Ultra V SAE 5W-30

diesel and gasoline engines. Oil samples were after flexible extended service intervals ranging from 14.000 km to roughly 33.000 km. Apart from the oil samples the auto service also provided the cars used with the specifications of their respective engines, the distance in kilometres covered by the various cars and the tachometers of the engines are shown in the table 3 below. All samples were homogenized by shaking for at least one minute before carrying out the experiment. All measurements were done under normal room temperature and each sample measured at least two to three times in order to get consistent results.

The following parameters were measured in all of the oil samples: Viscosity, Total Acid Number (TAN), Total Base Number (TBN), percentage of insoluble substance in used oil in pentane (ISP), carbon residue (MCRT), blotter spot test and FTIR spectrometry which was evaluated at an absorption area of organic nitrate. The organic nitrates were analysed at a wave length signal of around 1630 cm^{-1} . FTIR spectrum was measured on Nicolet analysis, type 740, path length of 0.1 mm.

Each and every measurement was carried out according to their respective norms.

Total Acid Number (TAN) and Total Base Number (TBN) were measured using the titration on an automatic titration apparatus Titrino DMS 716 (Metrohm Co.). The

used methods correspond to standards ASTM D2896 for TAN and ASTM D 2896.

Percentage of insoluble substance in used oil was measured by dissolving the sample in n-pentane diluted 30 times and then filtrated using $0.8\ \mu\text{m}$ filter from nylon fibre. Carbon residue was measured using micro (MCRT) according to ASTM D 4530.

The kinematic viscosity of the samples was measured Stabinger SVM 3000 automatic viscometer according to ASTM D7042 standard.

Nitrate content was measured using FTIR peak near 1630 cm^{-1} and the remaining detergency and dispersancy performance of the used oil was measured using the blotter spot test. Especially for TBN two methods were used;

Blotter spot test: This is based on the established procedure of paper chromatography and involves placing of couple of drops of used oil on a common blotter paper. The drop soak into the paper and spreads outwards, where the heavier particles mostly contaminants and soot are left in the centre as the lighter oil spreads from the centre outwards. Key indicators of soot are characterised by the size of the centre of the spot, colour of the centre of the spot, size of the diffusion zone, colour of the diffusion zone (black/gray), aureole formation mostly arising from incorrect injection condition and density or translucent and opacity of the spot [7, 11, 14, 16].

Results and discussion

Blotter spot test

Viscosity is a very important parameter of the oil that provides information about the degree of oxidation, thermal degradation and other changes taking place in the oil while it's in use. Increase in viscosity is caused mainly by thermo-oxidation changes that takes place in the oil and also partly by the evaporation of the volatile portion of the oil. Decreases in viscosity is mostly caused by the effect of thermal oxidation and shear stress on the polymer additives so called the viscosity modifiers or it can also be caused by dilution (mixing) of the motor oil with fuels. The mainly accepted changes in viscosity of oil while in service ranges between $20\div 30\%$ at 40°C and $20\div 25\%$ at 100°C relative to the new oil and vice versa. From table 4 and figure 3, the changes in viscosity at 40°C for most of the diesel and gasoline oil samples are lower or within the $20\div 30\%$ range relative to the new oil with one exception one gasoline oil sample surpassing the upper limit of the range. At 100°C , the changes

in viscosity for most of the samples are below or within the accepted limit of $20\div 25\%$.

The amount of carbon residue is a sign of the formation or tendency of the oil to form sludge which is attributed to the overheated areas of the engine. The amount of residue increases while the oil is in use due to the effects of sludge, varnish, dust particles and the formation of carbonic compounds, which is a result of the continuing oxidation and thermal degradation taking place in the oil. The accepted value of carbon residue is from the range of $3\div 3.5\%$ and it is often very good to use the upper limit for measuring the carbon residue in diesel engine oils because the formation of carbon residue in them is often more prominent than in gasoline engines. From the figure 5 and table 4 the carbon residue in all the samples are below or within the accepted range except in one case where the carbon residue level surpassed the upper limit of the range in both the diesel and gasoline oil samples.

From the figure 6 and table 4 above, two of the gasoline samples especially (26.000 and 29.802) have got increas-

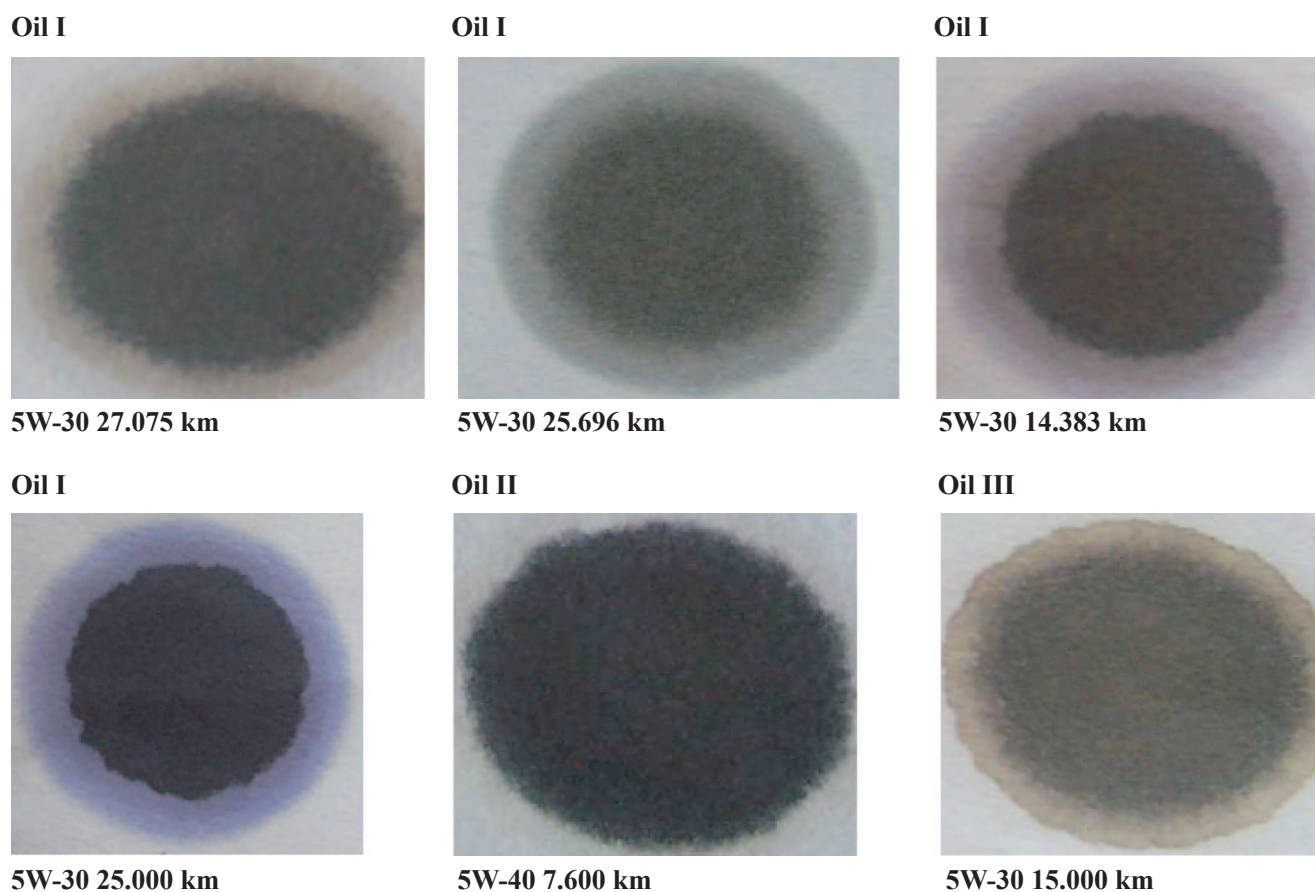


Figure 1. Pictures showing the appearance of the oil spots from low SAPS and other specifications at different drain intervals

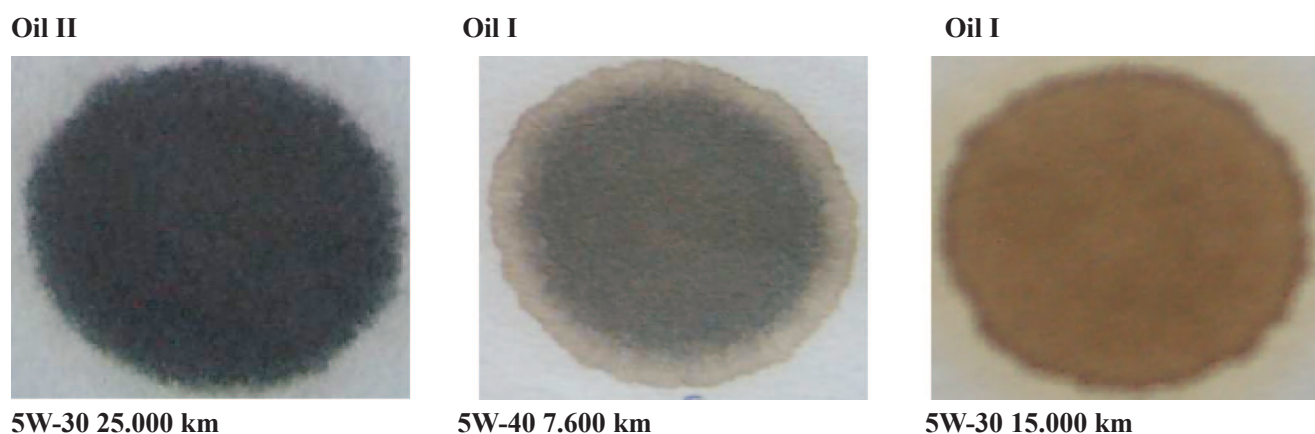


Figure 2. Comparison of spots taken from diesel and gasoline engines

ingly high amounts of insoluble substances in pentane as compared to diesel engine oil samples. The normal acceptable amount of insoluble substance in pentane is around 0.05% by mass maximum. New oil has zero insoluble substance in pentane.

There is a drastic decrease in TBN especially in both the diesel and gasoline engine oil samples (Figures 7, Table 4).

Most of the samples have TAN values much higher than the normal TBN value for new oil at 0 kilometres. The

condemning limit of TAN in relation to TBN is that, TAN value for used engine oil should not exceed or equal to the TBN of that same used oil. Here both gasoline and diesel engine oils have very high TAN values and that signals the degree of depletion of the alkaline reserves which is to neutralise the acids formed in the engine oil while in use.

New oil at 0 kilometres contains zero amount of nitrate. The maximum amount of nitrate in used oil that would not have much effect on TBN, TAN, pentane insoluble sub-

Table 4. Changes in the characteristics of the used low SAPS engine oil at their extended service interval in the different engines

Samples	Distance Travelled [km]	Viscosity (mm^2s^{-1})			MCRT [% (m/m)]	ISP [% (m/m)]	TBN ASTM D2896 [mg KOH/g]	SBN ASTM D4739-02 [mg KOH/g]	TAN [mg KOH/g]	Nitrate [ppm]
		40°C	100°C	VI						
1	14.383	67.45	11.8	160	2.30	0.054	5.75	2.30	6.20	17
2	21.000	63.33	12.4	169	3.10	0.025	5.10	2.90	5.20	28
3	21.000	73.10	13.1	154	2.70	0.034	4.70	2.40	5.80	5
4	25.000	84.96	12.0	168	2.70	0.026	5.40	2.00	5.90	0
5	25.696	70.24	10.7	160	2.60	0.034	4.20	1.80	6.20	47
6	27.075	79.83	11.7	167	2.40	0.038	3.80	2.00	5.10	10
7	28.907	68.53	12.6	166	2.40	0.032	3.90	2.00	5.70	3
8	29.036	82.71	13.4	164	2.70	0.025	5.60	2.70	6.00	12
9	29.491	75.77	12.3	159	3.50	0.028	5.10	3.00	5.80	9
10	29.828	64.60	11.1	165	2.70	0.035	5.00	3.00	6.30	0
11	30.000	65.61	11.2	164	2.30	0.029	2.80	1.60	5.50	57
12	30.262	75.77	12.5	166	2.80	0.031	5.60	3.00	5.90	6
13	31.152	81.02	13.2	164	2.90	0.038	5.90	2.90	7.70	4
14	31.563	60.47	10.8	171	2.20	0.030	5.20	3.20	4.10	18
15	16.016	74.34	11.8	154	2.50	0.022	3.00	3.00	6.30	107
16	26.000	63.02	13.4	171	3.40	0.096	3.80	2.00	5.90	184
17	29.802	90.68	13.5	150	3.00	0.092	1.30	1.30	6.10	168
18	30.320	74.91	11.9	159	3.10	0.018	1.60	1.60	6.50	205
19	33.719	73.47	11.5	149	3.20	0.049	2.80	1.60	5.90	110

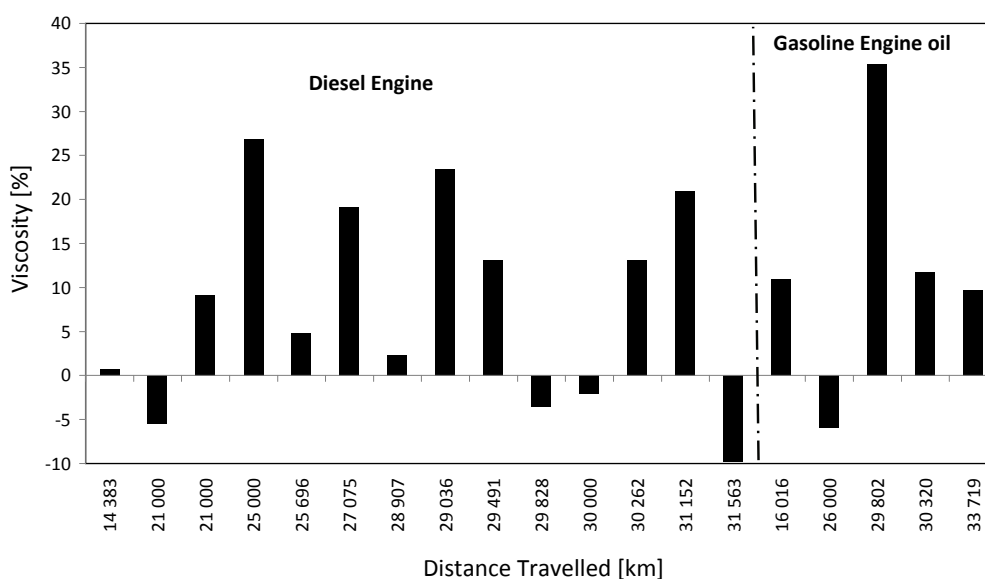


Figure 3. Relative percentage change in viscosity of the samples at 40°C

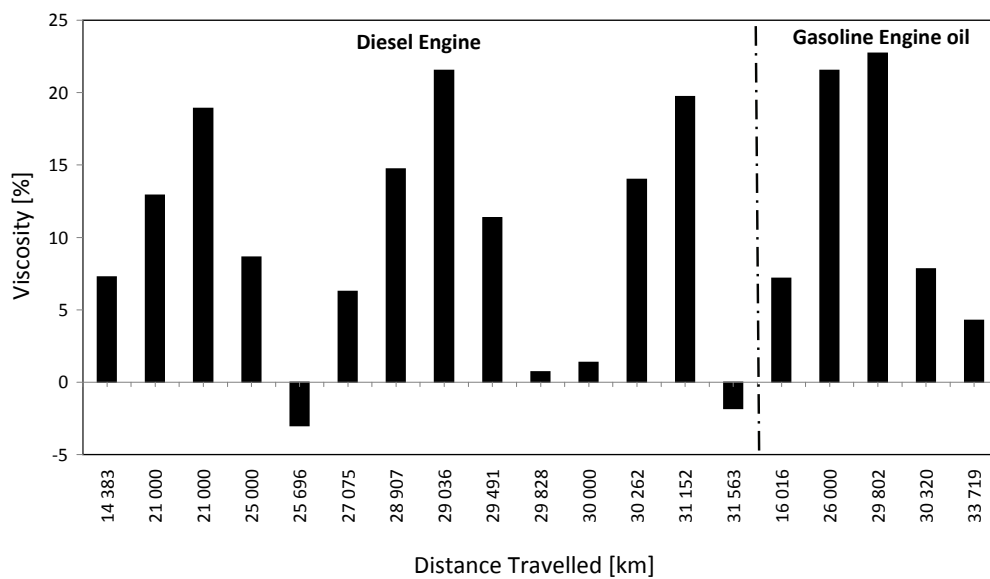


Figure 4. Relative change in viscosity of the samples at 100°C

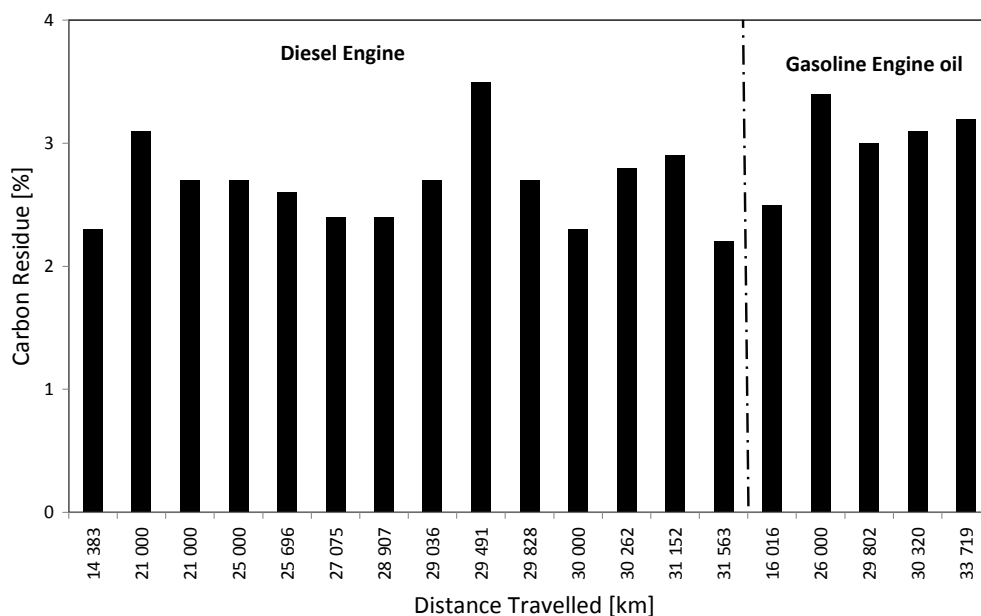


Figure 5. Carbon residue

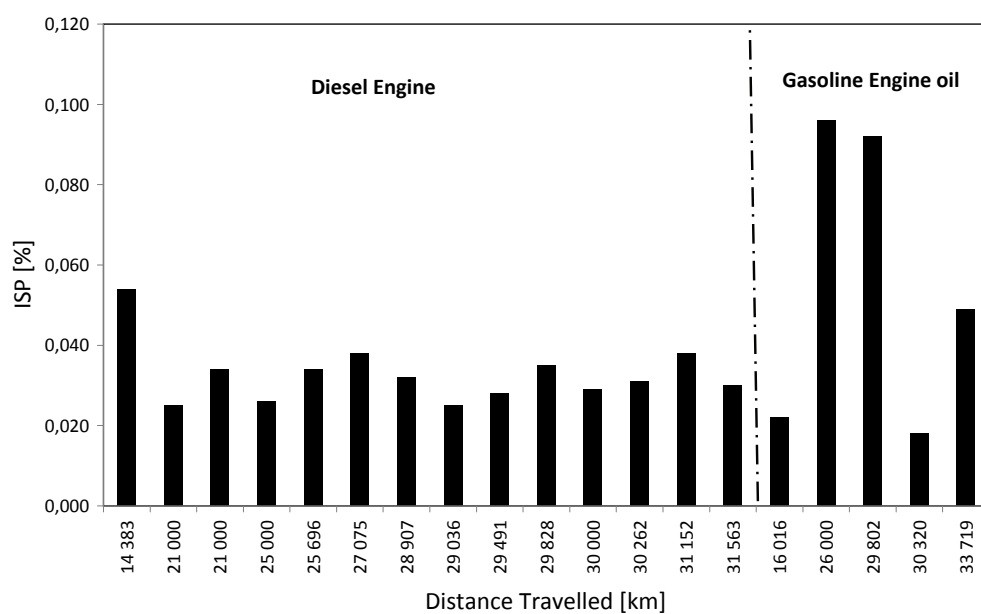


Figure 6. Insoluble substance in pentane (ISP)

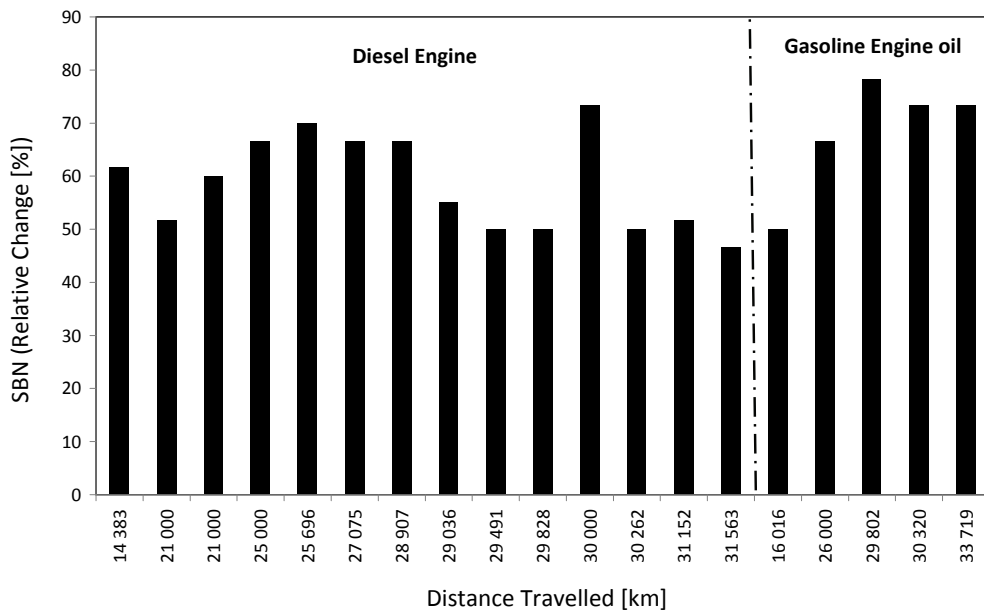


Figure 7. Relative change in SBN method ASTM D4739-02

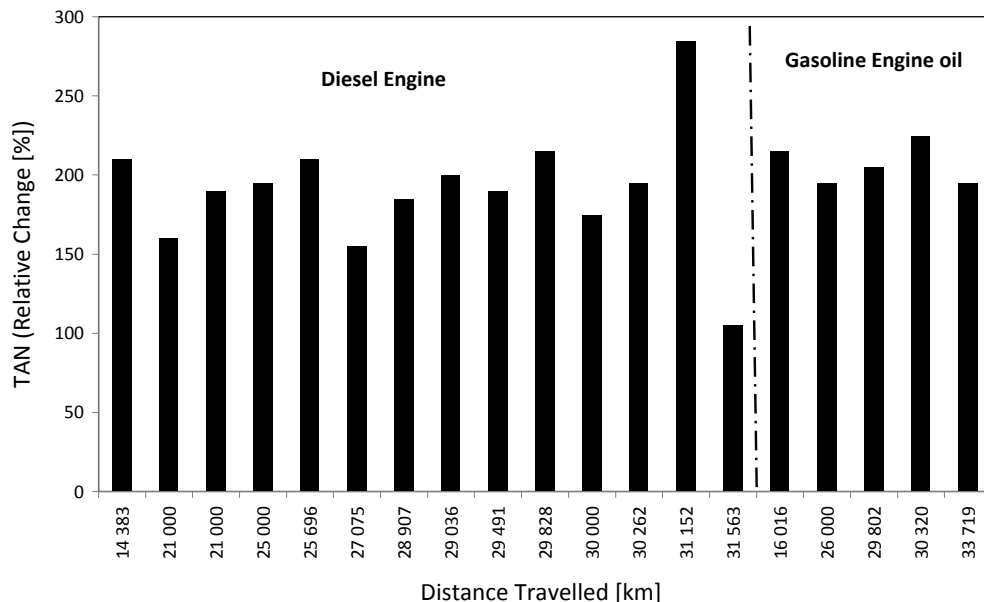


Figure 8. Relative change in TAN

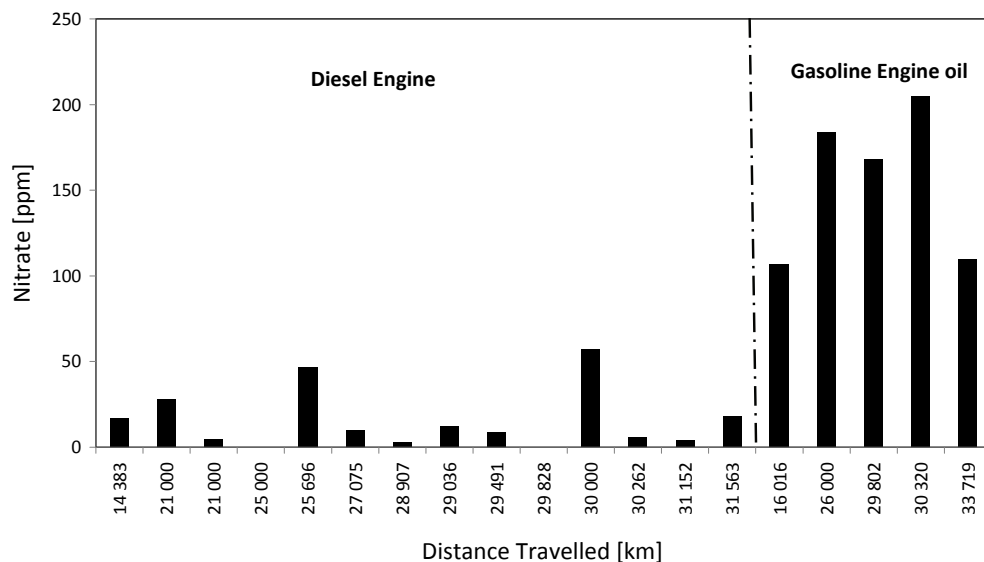


Figure 9. Nitrate content in the samples

stances etc. varies from oil to oil and also depends on the engine design and other factors that causes oil aging. The 250 ppm limit is the amount that would have an effect in the used oil in general. From figure 9 above, all the gasoline

engine oils contain high levels of nitrate but still well below the 250 ppm. All the diesel engine oil samples contains between 0 – roughly 50 ppm which is good especially for engine oils taken at 15.000 km – roughly 33.000 km interval.

Conclusion

The blotter spot method is a good method for the investigation of the dispersancy and detergency properties, amount of soot, and other contaminants in used engine oils. Clear results can be observed within hours to a day or two using an ordinary laboratory paper. However the longer the spot is left to stand in open, the clearer the result becomes. It is a simple method that can be carried out anywhere at home, in the field and doesn't require any special laboratory arrangement. The loss of detergency and dispersancy properties were clearly observed. Most of the samples showed serious depletions of detergency and dispersancy properties. From the above results the oils are more stable at 100°C than at 40°C.

The performance of the low SAPS motor oil here according to what we found out could be attributed to the way how the oil was changed. It should be noted that when changing the engine oil, the crank case should be totally emptied and cleaned thoroughly so that no contaminants like soot particles, wear debris, etc are left in it. The presence of these particles in the crank case would cause the premature deterioration and shortens the life cycle of the engine oil and therefore it would be inconclusive to attribute any changes that would occur in the oil to the real performance of the uncontaminated oil itself. Most time mechanics are not taking into account this problem seriously for the simple reason of saving time and money.

References

- [1] Barnes M.: *Elemental analysis*. Practicing oil analysis magazine, January, 25–27.
- [2] Batko M., Florkowski D.: *Lubricant requirements of an advance designed high performance, fuel efficient low emission V-6 engines*. SAE Tech. Pap. Ser. 2001011899.
- [3] Cerny J.: *Chemické rozborý motorových oleju*. Auto expert 2003, 8 (7-8), 26–29.
- [4] Cerny J.: *Mazaci oleje v každodenním živote*. Sborník 21, Letní Skoly, VSCHT Praha, 2007, 46–52.
- [5] Cerny J.: *Nova generace motorových oleju*. Chemické listy 2006, 100, 41–44.
- [6] Cerny J.: *Soucasný vývoj v oblasti motorových oleju*. Sborník 15. Conference Arochem, 24–26 Dubna 2006, Milovy, 1449–1454.
- [7] Cerny J.: *Zivotnost motorových oleju long life III*. Reotrib 2007m Velke Losiny, 30 Kvetna-1. Cervna 2007, 63–68.
- [8] CLS Control Lubricant service, ready reference field Guide, 2003.
- [9] Doyle D.: *Field Screening Methods for Soot Level in Used Diesel Engine Oils*. Lubricant Excellence Conference Proceedings, 2003.
- [10] Fitch J.: *The Lubricant field test and inspection guide*. Noria Corporation 2003.
- [11] Hala S.: *Hodnocení automobilových oleju*. Seminar 2008, analyza paliv, UTRAP.
- [12] Kalyan Kalyanaraman: *Let's talk about varnish, causes vary, but consensus is evolving on avoiding deposits*.
- [13] Mayer A.: *More test and what they tell us*. Technical Buletin No. 20, Wear Check Africa, 2001.
- [14] Mayer A.: *What a good on site oil analysis alb should look like*. Practicing oil analysis magazine July 2007.
- [15] Robinson N.: *Monitoring oil degradation with infrared spectrometry*. Technical Buletin No. 18, Wear Check Africa, 2000.
- [16] Sagi R., Bartha L., Beck: *Investigation of PIB – SUCCINIMIDES in engine oils*. Int. J. of Applied Mechanics and Engineering, 2006, vol. 11, No 3, pp. 507–513.
- [17] Troyer D.: *Get Ready for more soot*. Practicing oil analysis magazine, July 2003.



PhD Ing. Jaroslav CERNY – completed his M.Sc study in 1980 at the Institute of Chemical Technology in Prague and continued to a PhD studies at the same Institute and graduated in 1984. From 1994 till now – he works as a senior research scientist and senior lecturer in the field of analysis and chemistry of lubricant oils, tribodiagnostics of lubricated engines and devices.



Eng. Robert MAMGBI – finished his M.Sc studies in 2008 at the Faculty of Environmental technology, Institute of Chemical Technology in Prague. Currently he is a PhD student at the faculty of Chemical Engineering and Technology, Cracow University of Technology. Specialization – Oil and Gas Technology, Heterogeneous Catalysis and Hydrogen Fuel Technology.



Associate Prof. Erasmus BARIFAIJO – in 1985 he obtained M.Sc degree from the University of North Carolina at Chapel Hill, USA. In 2000 he completed his PhD in Geology at Makerere University Kampala Uganda. Currently he is an associate professor at Department of Geology and Petroleum Studies, College of Natural Science, Makerere University.