

COMPOSITION AND OXIDATION STABILITY OF SAE 5W-40 ENGINE OILS

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SUMMARY

Composition of base oils was studied by gas and liquid chromatography techniques after separation of additives from SAE 5W-40 engine oils. Ratio between hydrocracked oil and synthetic PAO was assessed from the GC chromatograms for semisynthetic engine oils or the fully synthetic basis of engine oils was confirmed. FTIR spectroscopic analysis of engine oils revealed a presence of esters as a part of base oils in some of the engine oils and approximate concentration of the esters was determined. Oxidation stability of the SAE 5W-40 engine oils was examined by using a modified high temperature oxidation test IP 48. Evaluation of oxidation tests was done by determination of some standard engine oil parameters, such as viscosity, carbon residue, and acid number. FTIR spectroscopy was used for determination of concentration increase of carbonyl bonds after oxidation tests. Fully synthetic engine oils mostly showed a better oxidation stability than semisynthetic oils. However, some fully synthetic engine oils exhibited decreased oxidation stability even in comparison with semisynthetic oils most likely due to an inappropriate choice of additive package.

Keywords: engine oils, base oils, properties, composition, oxidation stability

1 INTRODUCTION

Engine oils of the SAE 15W-40 specification are the most popular engine oils in most European countries. Due to climatic conditions these engine oils are satisfactory for a majority of car users. More demanding drivers and most of the car producers, however, require utilisation of lower viscosity oils, such as the SAE 10W-40 and SAE 5W-40 specifications. Differences between the SAE specifications mainly lie in low temperature properties, i.e. in cloud and pour point, and low temperature viscosity (CCS). However, there should be no significant differences in viscosity properties of the engine oils at their normal operational temperature.

The force of car producers to utilise the SAE 10W-40 and SAE 5W-40 engine oils is given by several factors. Very popular is the declared decrease in fuel consumption (Energy Conserving oils). However, fuel saving can only be apparent, in comparison with the SAE 15W-40 engine oils, at operation of cold engine, i.e. several minutes after cold start of the engine. Reliable decrease in fuel consumption can be reached by utilisation of the SAE 5W-30 and SAE 0W-30 engine oils. Ford and Volkswagen recently recommend those oils in Europe for new models of their motors. On the US and Japan market, there is even a new trend to assert the SAE 5W-20 and SAE 0W-20 engine oils [1].

Another factor supporting an enforcement of the SAE 5W-40 engine oils on the European market is their better pumpability and thus a better protection of engine parts against wear during cold starts. Lower viscosity of the oils also leads to an easier start at low temperatures below approximately -10 °C. One of the advantages of the SAE 5W-40 engine oils is a composition of their base oils. To reach high viscosity indexes, it is necessary to use PAO and/or hydrocracked VHVI base oils for a production of these engine oils.

Such oils contain no or very small concentration of aromatic hydrocarbons and, therefore, their tendency to form sludge and varnish is minimised. It helps to keep engine parts clean. On the other hand, the SAE 15W-40 engine oils are mostly produced from conventional solvent refined base stocks and their increased content of aromatics, up to about 30 wt %, can cause an extensive sludge and solid deposit formation during the oil life.

For European customers, there is one significant disadvantage of the SAE 5W-40 engine oils, namely their high price. Despite the practical reasons for utilisation of the SAE 5W-40 engine oils the economical aspects thus play a very important role in deciding of drivers which engine oil to use in their car. Usage of the SAE 5W-40 engine oils can be advantageous in new cars mainly in cases when *i*) it is necessary to maintain reliable start ability of an engine at low outdoor temperature in winter, *ii*) annual mileage is greater than about 15 000 km, and *iii*) oil is often exposed to the stop-and-go driving, particularly with cold engine.

This work is aimed at a comparison of oxidation stability of the SAE 5W-40 engine oils from different producers as oxidation stability is one of the important oil properties influencing on the oil life. An attention was also paid to analysis of the oils with the goal to assess the composition of base oil used for the production of SAE 5W-40 engine oils.

2 EXPERIMENTAL

2.1 Samples

Samples of the SAE 5W-40 engine oils were collected in 1999 from the official distributors in the Czech Republic. List of the oils is shown in Table 1.

Engine oil	SAE	API	ACEA	PAO (%rel)	HC (%rel)	Ester (wt%)
Aral High Tronic	5W-40	SJ/CF	A3/B3	75	25	0
BP Visco 5000	5W-40	SJ/CF	A3/B3	40	60	0
Castrol TXT Softec Plus	5W-40	SJ/CF	A3/B3	25	75	0
Elf Synthese	5W-40	SJ/CF	A3/B3	100	0	0
Esso Ultron	5W-40	SJ/CF		100	0	10.0
Mobil 1	5W-50	SJ/CF	A3/B3	100	0	23
Mogul Forte Racing	5W-40	SH/CF	A3/B3	100	0	4.0
Mogul Forte Racing New	5W-40	SH/CF	A3/B3	75	25	0
ÖMV full syn	5W-40	SH/CD	A3/B3	100	0	4.0
ÖMV syn com	5W-40	SJ/CF	A3/B3	75	25	0
Pennzoil Performax	5W-40	SJ/CF	A3/B3	100	0	0
Shell Helix Ultra	5W-40	SJ/CD	A3/B4	0	100	8.5
Texaco Havoline Formula 3	5W-40	SJ/CF		100	0	0
Total Quartz 9000	5W-40	SH/CF		100	0	8.5

Table 1: List of the SAE 5W-40 engine oils tested and analysis of their composition

2.2 Analysis of oil composition

Engine oils were first fractionated by size exclusion chromatography on Bio-Beads SX3 polystyrene-divinyl-benzene gel with mixture of toluene/ ethyl-alcohol 9:1 v/v [2]. Oil fraction free of viscosity modifiers were further fractionated on dual silica-alumina column with hexane, toluene, and a mixture of polar solvents [3] to give fractions of saturated hydrocarbons, aromatics, and polar compounds. All additives and ester base oil were concentrated in the polar fraction.

Fraction of saturated hydrocarbons were analysed by gas chromatography on a 12 m long capillary column. Fresh oils were analysed by FTIR spectroscopy in a 0.1 mm KBr cell without solvent.

2.3 Oxidation test and evaluation

Oxidation test was based on the IP 48 standard method. The standard method was modified for oxidation of formulated engine oils. Test temperature was maintained at 200 °C and flow rate of air was 15 l h⁻¹. The only parameter different from the IP 48 test was the oxidation time which was prolonged from 12 hours to 35 hours. Engine oils were oxidised in five 7 h-cycles within one week. Oxidations were performed in commercial apparatus Analis with heated aluminium block.

Fresh as well as oxidised oils were measured for evaluation of the following parameters: kinematic viscosity at 40 °C and 100 °C (ASTM D445), viscosity index (ASTM D2270), Micro carbon residue (MCRT, ASTM D4530), and acid number by potentiometric titration (ASTM D664). Fresh and oxidised oils were also analysed by FTIR spectroscopy in 0.1 mm KBr cell, and intensity of carbonyl absorbance was evaluated.

3 RESULTS AND DISCUSSION

3.1 Composition of SAE 5W-40 engine oils

Size exclusion chromatography, the first fractionation step, led to an assessment of viscosity modifiers quantity in the engine oils. Amount of viscosity

modifiers was found in the range between 3.8 wt. % and 7.7 wt. %. Most of the oils had, however, amount of viscosity modifiers in the range from 5.5 wt to 7.7 wt. %. Viscosity modifiers from individual engine oils were qualitatively analysed by FTIR spectroscopy, and it was examined that all viscosity modifiers were either olefin copolymers or hydrogenated styrene-diene copolymers. Polymethylmethacrylates were not detected in any of the oils.

Aromatic hydrocarbons were found in each oil, even in the fully synthetic oils. Origin of aromatics in fully synthetic oils can come from the additive package, in which the additives were dissolved in solvent neutral oils. Amount of aromatics in engine oils was mostly below 5 wt %.

Fraction of saturated hydrocarbons was analysed to confirm the synthetic nature of the fully synthetic engine oils or to assess the ratio between the PAO and hydrocracked oil content. As can be seen in Figure 1, PAO and hydrocracked oils give quite different signal in chromatograms. So, mixtures of PAO and hydrocracked oils (25:75, 50:50, and 75:25 w/w) were prepared and chromatograms obtained were used to assess a proportion of the components in base oils of the semisynthetic engine oils.

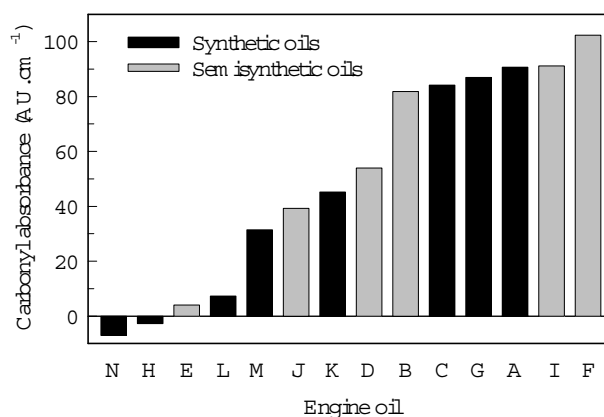


Figure 1: GC chromatograms of PAO 6 and hydrocracked base oil

On the basis of comparison of the shape of chromatograms of standard mixtures and the shape of chromatograms of saturated fractions, the composition of base oils was assessed and results are shown in Table 1. Amount of esters in base oils also shown in Table 1 was determined from the FTIR spectra evaluation and from quantity of polar compounds after adsorption chromatography of engine oils.

The oil Shell Helix Ultra was declared by the producer as fully synthetic oil. However, detailed analysis proved that its base oil was made from a mixture of hydrocracked oil, most likely hydroisomerised slack wax, and ester oil, and it is further referred to as semisynthetic engine oil.

3.2 Oxidation stability of SAE 5W-40 engine oils

Evaluation of oxidation stability according to selected oil parameters is shown in Figures 2 to 6. Individual oils were ordered in the Figures so that the oils with the smallest oxidation changes were placed at the left side and successively followed by oils with large oxidation changes. Oils with the largest oxidation change were always at the right side of the Figures.

Viscosity changes after oxidation are shown in Figure 2. The most stable oils had negligible viscosity increase after oxidation. Some of the oils even showed viscosity decrease caused by thermal cracking of polymeric viscosity modifiers while only minor oxidative changes leading to oil thickening occurred. On the other hand, two of the engine oils, namely the synthetic ones, showed significant viscosity increase.

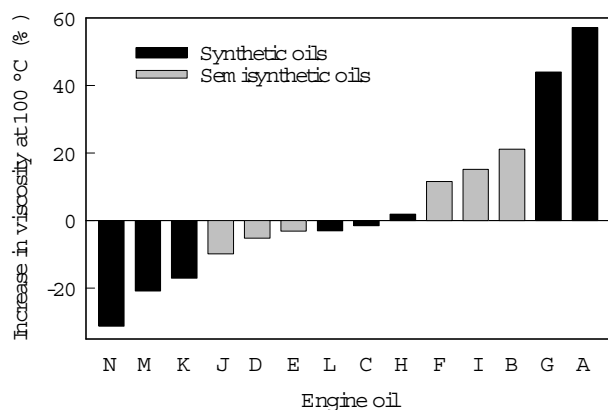


Figure 2: Changes in viscosity at 100 °C after oxidation of SAE 5W-40 oils

Changes in viscosity at 100 °C (Figure 3) after oxidation of the engine oils were smaller than in the case of viscosity at 40 °C. Reason can be seen in that the effect of degradation of viscosity modifiers is more marked at the higher temperature. Viscosity at 100 °C has, therefore, less significance for evaluation of oxidation stability than viscosity at 40 °C [1,2].

Viscosity index was for all oxidised oils smaller than that for fresh engine oils. Drop of viscosity index was about 5 % for the most stable oil (Oil E) and about 25 % for the Oils I, C, and J.

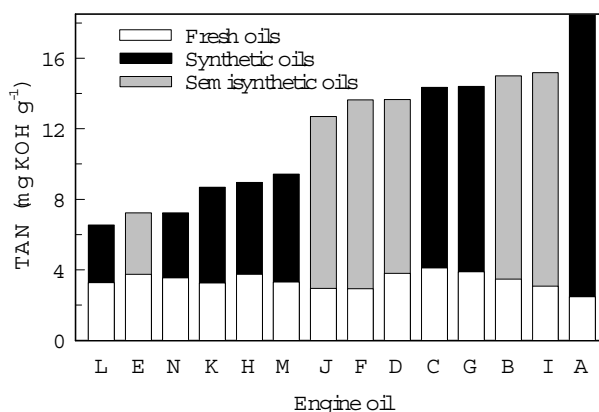


Figure 3: Changes in viscosity at 100 °C after oxidation of SAE 5W-40 oils

Micro carbon residue of the oxidised oils is shown in Figure 4. Amount of carbon residue was very similar for all fresh oils, slightly above 1 wt. %. After oxidation, carbon residue amount was approximately twice as high. Carbon residue of the less stable engine oils was increased even up to 4 wt. %.

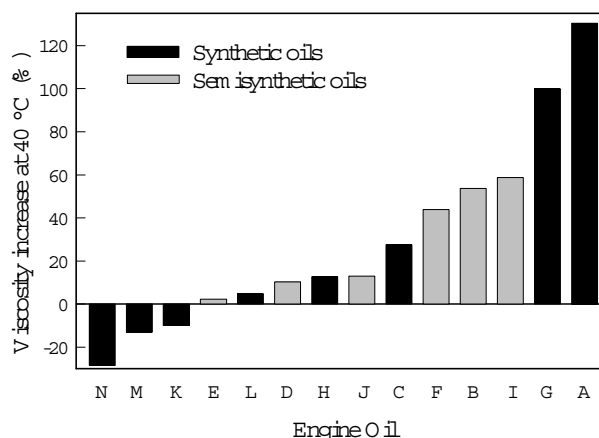


Figure 4: Increase in Micro carbon residue after oxidation of SAE 5W-40 oils

Acid number is very illustrative parameter of oxidative changes in oxidised oils. Its values for fresh as well as oxidised engine oils are shown in Figure 5.

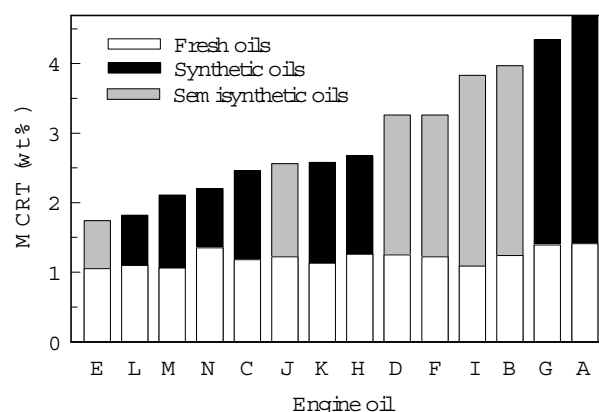


Figure 5: Increase in acid number after oxidation of SAE 5W-40 oils

Again, very different increase of that parameter was found after oxidation of the SAE 5W-40 engine oils. The most stable oils showed only about 3 mgKOH g⁻¹ increase in the acid number, while the increase for Oil A was very significant.

Also amount of carbonyl groups in oxidised oils was very different depending on the engine oil. The most oxidation stable oils showed only negligible changes in carbonyl absorbance measured by FTIR spectroscopy.

3.3 Oxidation stability of synthetic and semisynthetic oils

It can be seen in Figures 2 to 6 that fully synthetic engine oils mostly showed better oxidation stability than semisynthetic oils. It can be thus understood that synthetic oils have a higher potential for prolongation of the oil drain interval. This proposition, however, cannot be generalised. There were some semisynthetic oils in the analysed set of oils that were oxidatively very stable and at least comparable to fully synthetic oils. That is especially the case of Oil E and also Oils D and J. On the other hand, oxidation stability of some synthetic oils, e.g. Oils A and G, was lower than that of semisynthetic oils.

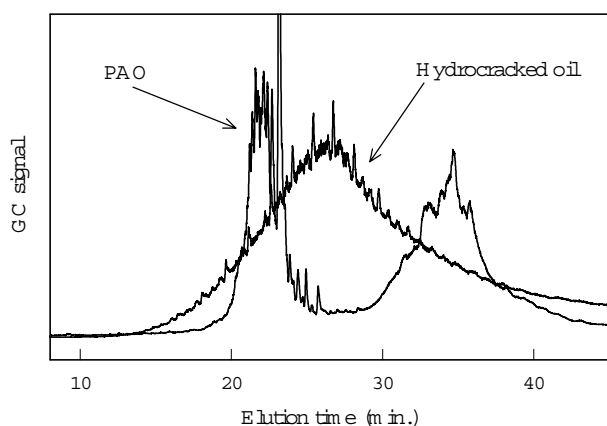


Figure 6: Change in carbonyl absorbance after oxidation of SAE 5W-40 oils

It is often reported that synthetic PAOs have better response towards antioxidants than oils containing aromatic hydrocarbons and sulphur. Fully synthetic engine oils are thus more oxidatively stable than semisynthetic and mineral engine oils. Results obtained in this work mostly supported that statement. Nevertheless, the key point in oxidation stability of engine oils is a harmonisation of additive package with the actual base oil. Good additivation of semisynthetic base oil can also lead to a very stable engine oils (see the Oils E and D in Figures). Due to an existence of the optimum aromaticity, the optimal concentration of

aromatics and sulphur compounds in a base oil should theoretically lead to an engine oils with the highest oxidation stability, of course under the assumption of successful optimisation of the additive package [4]. However, harmonisation of additive package with base oil is much more easy for chemically uniform PAOs than for hydrocracked or even solvent neutral base oils. Composition of mineral oils is highly dependent on the refining technology and differs from one producer to another. Serious problem of hydrocracked base oil is their different content of aromatics and sulphur which leads to problematic interactions with additive compounds and makes it difficult to optimise additive package [5, 6]. Modern technologies are therefore directed to produce clear and aromatics and sulphur free base oils. An example of such technology is the Chevron tree-stage hydrorefining process, which produces clear colourless hydrocracked oils free of aromatics and sulphur and with a polyaromatic hydrocarbons content near the limit of determination.

4 ACKNOWLEDGEMENT.

The work was supported by the Grant Agency of the Czech Republic under the Grant Agreement No. 104/00/0576. Authors also thank Koramo a.s., Kolin, for support of the work.

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