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ENGINE OIL VISCOSITY INDEX IMPROVER BEHAVIOUR AT EXTENDED SHEAR STABILITY TEST

Abstract

Multigrade engine oils among numerous additives, always contain also viscosity index improvers. These additives are special types of polymers, which in small concentration significantly improve engine oils rheological properties, especially viscosity and viscosity index. However, during engine oils utilization, degradation of viscosity index improvers ie. break down of polymeric molecules occures. It results in reduction of their molecular weight what leads to viscosity loss and oil film thickness decrease, which causes undesirable phenomena of friction and wear.

The shear stability of the viscosity index improvers that is the polymer resistance to mechanical degradation under shear stress is determined by measuring of the viscosity loss after repeated oil passing through the injector nozzle. The engine oil specifications define the minimal oil viscosity grade after the shear.

By introducing the new ACEA and API specifications, the requirements for the shear stability of engine oils have been changed and now they are accepted by engine and vehicle manufacturers. In order to achieve better correlation with engine oil application results, it is defined that the shear stability should be determined by standardized apparatus extending current testing of 30 to 90 cycles of oil passing through the nozzle.

The paper presents the shear stability testing of most important types of commercial viscosity index improvers on Orbahn diesel injector apparatus at extended shear stability test (90 cycles) with aim on meeting the new engine oil specifications.

1. Introduction

The primary role of engine oil is the lubrication of moving engine parts and reducing friction and wear of metal surfaces which provides the good engine performance and its long life. In order to provide a defined quality of engine oils during production and for final products to meet the product specifications we need to know the physical-chemical characteristics of engine oils.

Certain physical-chemical characteristics which are significant for the quality of engine oils are achieved by adding additives to base oils. The most frequent additives are for:

- Improving of viscosity index-improvers
- Reducing pour point-depressants
- Maintaining engine cleanness-detergents and dispersants
- Preventing oxidation-antioxidants
- Preventing corrosion-corrosion inhibitors

The most important engine oils characteristic is the viscosity defined as a measure of inner friction which works as a resistance to the change of molecule positions in fluid flows when they are under the impact of shear force, or in other words, it is the resistance of fluid particles to shear. When fluids flow, there are friction forces between their particles and also between fluid particles and the adjoining surface, caused by the resistance of fluid to particle shear and also of surface roughness. The viscosity is a changeable category and it depends on the change of temperature and pressure. A higher temperature reduces the viscosity and makes a fluid thinner.

The viscosity index is an empirical number which shows how the viscosity of some oils changes by increasing or reducing the temperature. High viscosity index shows relatively small tendency of viscosity to change upon influence of certain temperature, as oppose of low viscosity index which shows greater viscosity change with temperature. The calculation is based on viscosity values determined by ASTM D 445 method at 40 and 100 ℃.

2. Additives for viscosity index improvement

The viscosity index improvers impact the oil behaviour as far as flow characteristics are concerned. The sensitivity of viscosity index improvers to mechanical stresses increases with increasing of polymer additives molecular weight. High shear stress causes the irreversible molecular degradation of polymers and reduces their molecular weight. This reducing of an average molecular weight results in reducing the viscosity and viscosity index [1,2].

Colloidal systems are created by dissolution of polymeric viscosity index improvers in mineral oil. They have different physical properties depending on the nature and length of molecules and also on the type of a solvent. These properties are defined by shape, conformation of dissolved molecules and their variation in temperature.

There are two forces influencing dissolved polymer molecules:

- Intramolecular forces-within a molecule. The result of their activity is that molecules form coiled conformation of small hydrodynamic volume which insignificantly increases viscosity.
- Intermolecular forces-between polymer molecules and a solvent. By their increase intramolecular interactions are reduced, polymer molecules form elongated conformation of large hydrodynamic volume which leads to viscosity increase.

All the mentioned mechanisms are affected by temperature, quality of polymer solvent and molecular weight of polymers. The efficiency of a solvent depends on its similarity with chemical structure of polymers. For the same quantity of polymers dissolved in different solvents, a higher viscosity is a result of a good solvent rather than the temperature. The solubility of polymers in oil decreases with its molecular weight increase [2,3].

Additives for the viscosity index improvement influence the following characteristics of multigrade engine oils [3]:

- at low temperatures they maintain the oil sufficiently liquid, which means when starting the engine with low internal friction, just the minimal engine power is used and it provides a safe engine starting,
- at high temperatures they give the oil higher viscosity which provides a necessary oil film thickness and a small oil consumption.

The most known polymer additives for viscosity index improvers are:

- polymethacrylates (PAMA),
- olefin copolymers (OCP),
- hydrogenated styrene-dien copolymers.

2.1 Polymethacrylates (PAMA)

Polymethacrylate additives are polymers based on long chain esters of methacrylic acid (C_8-C_{20}) made by free radical polymerization of appropriate monomers.

Apart from increasing viscosity and viscosity index, these polymers can also have pour point depressant properties which are achieved by implementing long-chain alkylate groups into their molecular structure. Long-chain alkylate groups of methacrylate additive co-crystallizing with long-chained paraffins present in mineral base oil, prevents the generation of paraffinic crystal clusters and gels, enabling flow at lower temperatures [1,3].

The viscosity index improvers based on polymethacrylates which are used for engine oils have molecular weight between 250000 to 750000 g/mol [1,4].

2.2 Olefin copolymers (OCP)

Olefin copolymers are copolymers of ethylene and propylene. A mass content of ethylene in OCP is 40-60 % m/m. The optimized ethylene-propylene ratio significantly contributes to thickening efficiency and low temperature solubility. A higher content of ethylene increases the viscosity of a solvent, but too much of it leads to polymer crystallization and insolubility at low temperatures. So, copolymers with too high ethylene content increase the tendency to create crystal structures with paraffin hydrocarbons of mineral base oils and thus they reduce oil flow rate. Also, because of low oxidation stability it is desirable to minimize the content of propylene to achieve the best possible properties [1,2].

Apart from good properties of the viscosity index improvement, OCP also possess good solubility and thermal stability. Due to its excellent thickening ability, OCP has an important application in engine oils.

The OCP viscosity index improvers do not possess properties of pour point depressants. For that purpose they are mixed with 2-3 % of conventional pour point depressants [1].

The viscosity index improvers based on OCP have molecular weight from 50000 to 200000 g/mol [1,4]. A big advantage of OCP viscosity index improvers, in comparison to other viscosity index improvers, is their low price.

2.3 Hydrogenated styrene-diene copolymers

Depending on the type of present diene, there are styrene-butadiene (SBC) and styrene-isoprene (SIP) polymers. They have the optimized molecular weight which resists shear stresses when used in engine oils [1,2].

Styrene-isoprene copolymers have good high temperature and low temperature properties (pumpability). The molecular weight of styrene-isoprene polymers is between 50000 and 100000 g/mol [1,4]. They are most widely used in engine oils. They can also be used in other fields of appliation with more stringent requirements for shear stability, for example as tractor transmissions fluids and airplane piston engine oils.

3. Shear stability

Shear stability is usually defined as the resistance of polymers to mechanical degradation under the shear stresses and it depends on molecular weight and a chemical nature of polymer additive. With higher molecular weight of polymer, there is greater possibility of their breakdown.

When used, polymers that are exposed to high shear stresses show molecular degradation. Shear process is a simple homolytic splitting of carbon-carbon bond in two polymer radicals [2].

Shear stability is determined by measuring of the viscosity loss after repeated oil passing through the nozzle. The formula for the viscosity loss is:

$$\text{Viscosity loss (\%)} = \frac{\nu_1 - \nu_2}{\nu_1} * 100$$

where: ν_1 = kinematic viscosity of fresh oil
ν_2 = kinematic viscosity of sheared oil

4. Engine oil specifications

Engine oil specifications serve engine and vehicle manufacturers, lubricant and additive producers and consumers of engine oils. They are defined in order to provide the necessary engine oil quality for lubrication of modern engine design. One of the specification requirements is the shear stability of engine oils.

For determining shear stability we use DIN 51382 method which is also accepted by CEC as the CEC L-14-A-93 method and by ASTM as the ASTM D 6278 method. These are a part of the international specifications for engine oils. The viscosity loss due to shear stresses is normally determined after 30 cycles of oil passing through the nozzle.

During engine oils application, its viscosity is decreased due to polymer break down of the viscosity index improvers which reduces oil film thickness and causes undesirable phenomena of friction and wear. For this reason, specifications for engine oils containing polymer additives, define the minimal value of kinematic viscosity after shearing (Table 1) [5].

Table 1: SAE J300 May04 – Kinematic viscosity at 100 °C

SAE viscosit grade	Kinematic viscosity at 100 °C mm^2/s	
	nin	ıax
XW-20	5,6	9,3
XW-30	9,3	12,5
XW-40	12,5	16,3
XW-50	16,3	21,9

The manufacturers of vehicles and equipment OEM (Original engine manufacturer) pointed out that the current test for shear stability of engine oils at high loaded diesel engines does not provide satisfactory results and therefore there is not sufficient equipment protection while under application. They believe that this is a consequence of high sliding speeds, heavy loads and high working temperatures where the oil is exposed to the high shear which results in viscosity loss, reduced the oil film thickness and impaired lubrication. The oil does not provide a sufficient viscosity for the engine protection.

In order to find a suitable solution, it has been proposed to perform shear stability testing with already known Orbahn Diesel Injector apparatus. An agreement is reached to expend testing from 30 cycles to 90 cycles which would be better comparable to conditions in practical application.

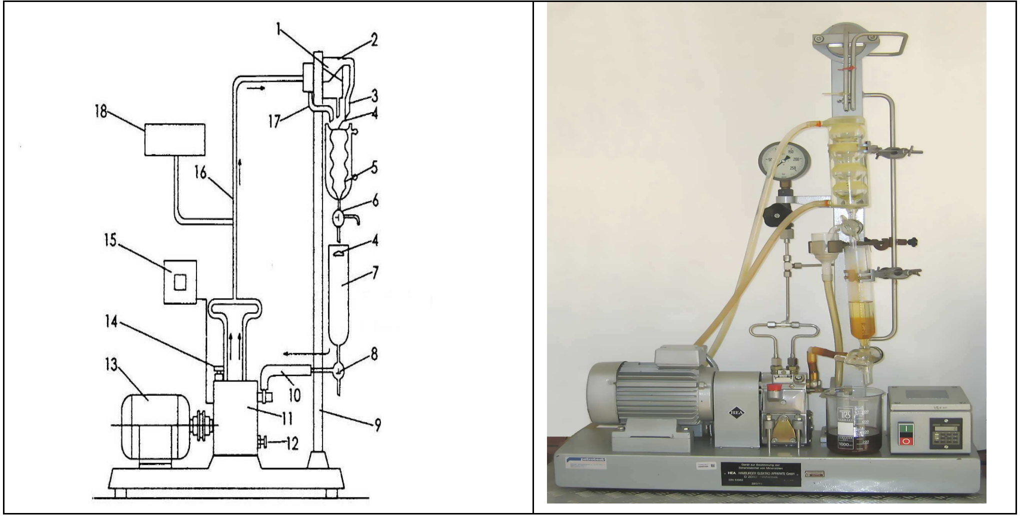
The new ASTM D 7109 method for shear stability testing has been established which differs in more testing cycles and sample quantity than the previous ASTM D 6278 [6,7].

By introduction of the new ACEA (Association des Constructeurs Européens d'Automobiles) and API (American Petroleum Institute) specifications, the changes in requirements for determining shear stability of engine oils aroused. The new ACEA E6-04 and E7-04 specifications than API CI-4 Plus and API CJ-4 set more stringent requirements for the shear stability with the use of the same method, but with 90 cycles instead of the previous 30 cycles of testing [5].

Apart from ACEA and API specifications, determining shear stability of oils with 90 cycles tests, is also required by some engine and vehicle manufacturers, for example, Mercedes-Benz – all the specifications, Volvo for VDS-3 and VDS-4 and other manufacturers in relation to ACEA and API specifications.

All of them require that kinematic viscosity at 100 ℃ after shearing remains within SAE J300 classification grades (Table 1).

Figure 1: Apparatus for shear stability testing



Parts of the apparatus:

1. Spray nozzle
2. Atomization chamber
3. Outlet of the atomization chamber
4. Distributor plate
5. Fluid cooling vessel
6. Three-way cock cooler downstream
7. Glass fluid container
8. Three-way cock container downstream
9. Support column
10. Connection with pump-suction opening
11. Double-plunger injection pump
12. Pump setting screw
13. Electric motor
14. Venting screw
15. Counter
16. Pressure pipe from pump to injector
17. Return line for overflowing liquid
18. Pressure sensing device

5. Experimental

Apparatus for shear stability testing

Determining shear stability is performed on Orbahn Diesel Injector apparatus (Figure 1) [6,7,9]. The apparatus consists of an electric motor which drives a double plunger injection pump, spray nozzle, an atomization chamber, fluid cooling vessel, a glass fluid container, pressure sensing device and stroke counter.

A sample of the tested oil (200 cm^3) is submitted to shear stress which is performed under the specific conditions of pressure, temperature and a specific number of cycles. Oil passing through the spray nozzle with high shear speed causes the degradation of less shear stable polymer molecules.

In order to establish the viscosity loss, the kinematic viscosity of fresh oil ν_1 and sheared oil ν_2 is determined by ASTM D 445 at 100 ℃. Determining the kinematic viscosity is performed by measuring time of passing of a particular fluid volume through the calibrated glass capillary viscometer under gravity influence and exactly controlled temperature. The value of kinematic viscosity is obtained by multiplying the time of fluid passing with a viscometer constant (mm^2/s). The reduction of kinematic viscosity, or in other words, the percentage of the initial kinematic viscosity loss of oil is a measure for the shear stability of oils containing polymers.

6. Test results and discussion

The testing of shear stability of multigrade engine oils was performed by ASTM D 7109 method on samples with SAE 15W-40 viscosity grade. The same additive package (DI) has been used, with the same initial values for kinematic viscosity at 100 ℃ ($KV_{100} = 14,5 \pm 0,1$ mm^2/s) and dynamic viscosity at -20 ℃ ($CCS_{-20} = 6\,650 \pm 50$ mPa·s), but with addition of three types of commercial viscosity index improvers.

The viscosity index improvers based on polymethacrylates (A), olefin copolymers of different manufacturers (B1, B2, B3 and B4) and styrene-isoprene copolymers (C) were compared. The aim of testing was to determine if the mentioned viscosity index improvers with extended test of shear stability (90 cycles) meet requirements of the new engine oil specifications.

The research is performed in two phases. For determining of viscosity loss the sample has been taken after 30 and 90 cycles.

Table 2 show test results of the engine oil shear stability depending on type and concentration of polymeric viscosity index improvers.

The data from the table 2 show that for the formulating of engine oils with conditions given in advance, the kinematic viscosity of base oils at 100 ℃ of certain samples did not differ significantly (0 – 0,37 mm^2/s) which is shown on Figure 2. Simultaneously, the concentration of viscosity index improvers was quite different (Figure 3) and significantly bigger for improvers based on OCP in relation to those improvers based on polymethacrylates (A) and styrene-isoprene (C).

Table 2: Test results of engine oil shear stability

Property	Viscosity index improver						Method
	A	B1	B2	B3	B4	C	
Viscosity index improver concentration, % (m/m)	6,9	9,3	9,2	9,2	9,3	6,4	—
Kinematic viscosity of base oil at 100 °C, mm^2/s	5,62	5,52	5,52	5,54	5,75	5,89	ASTM D 445
Kinematic viscosity of engine oil at 100 °C, mm^2/s	14,44	14,45	14,44	14,60	14,56	14,41	ASTM D 445
Shear stability KV at 100 °C after shearing, mm^2/s Viscosity loss after 30 cycles, %	12,53 13,23	13,19 8,72	13,05 9,63	13,44 7,94	13,15 9,68	13,47 6,49	ASTM D 7109
Shear stability KV at 100 °C after shearing, mm^2/s - Viscosity loss after 90 cycles, %	12,35 14,17	12,91 10,66	12,82 11,22	13,16 9,86	12,93 11,20	12,38 14,09	ASTM D 7109

The test results show the expected degradation of tested oils due to decrease of kinematic viscosity (Figure 4).

The samples B1, B2, B3 and B4 based on OCP show very good stability to shear stresses and they meet the requirements of the shear stability with 90 cycles of testing, i.e. the engine oil remains within viscosity grade.

The samples A and C, which met the specification requirements with 30 cycles of testing, after testing shear stability with 90 cycles show the kinematic viscosity loss under the limit value of 12,5 mm^2/s. Therefore they do not meet the requirements of the new specifications of engine oils.

After extension of testing, kinematic viscosity loss of sample A is not large and amounts 0,18 mm^2/s (Figure 5). In order to achieve the minimal kinematic viscosity required by the new engine oil specifications, the initial kinematic viscosity at 100 °C should be increased for oils mixed with the viscosity index improvers based on polymethacrylates.

The sample C has shown a great viscosity loss after being tested with 90 cycles. That loss is 1,09 mm^2/s, which is significantly more than with other samples where it amounts 0,18 – 0,28 mm^2/s (Figure 5). This shows that the viscosity index improvers based on styrene-isoprene are not suitable for formulating the most demanding engine oils.

The test results demonstrate that the oils formulated with inappropriate viscosity index improvers are not able to provide the proper protection of an engine.

Figure 2: Kinematic viscosity of base oil at 100 ℃

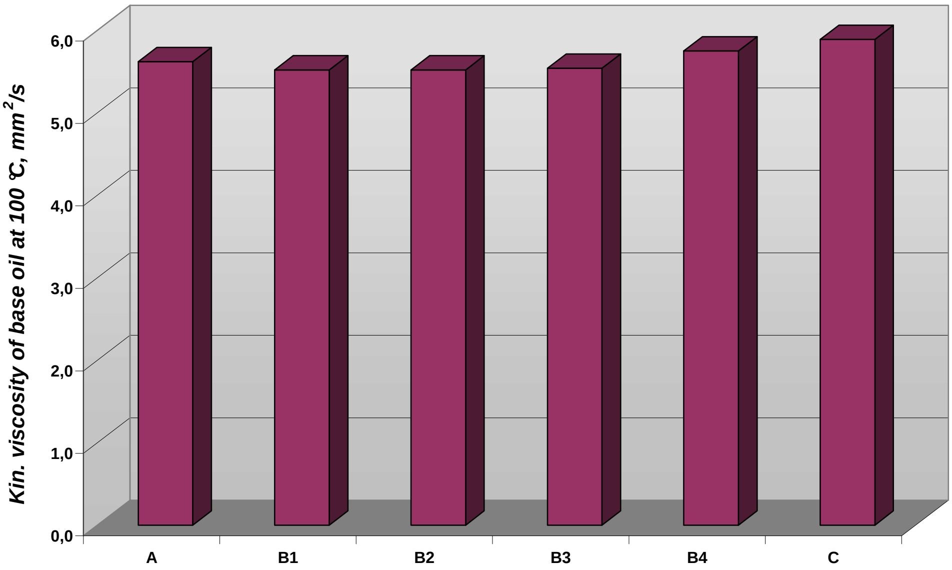


Figure 3: Concentration of viscosity index improver in oil

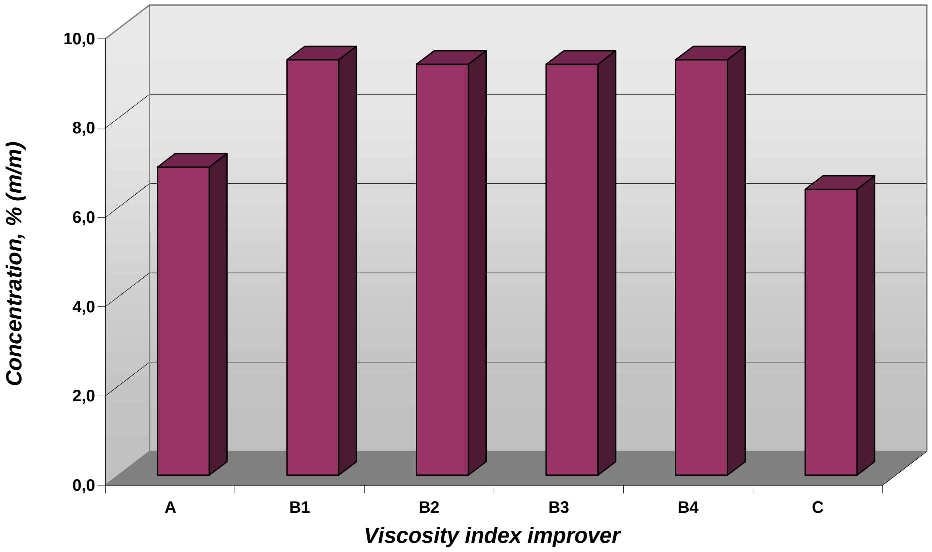


Figure 4: Kinematic viscosity at 100 ℃ after 30 and 90 cycles of testing

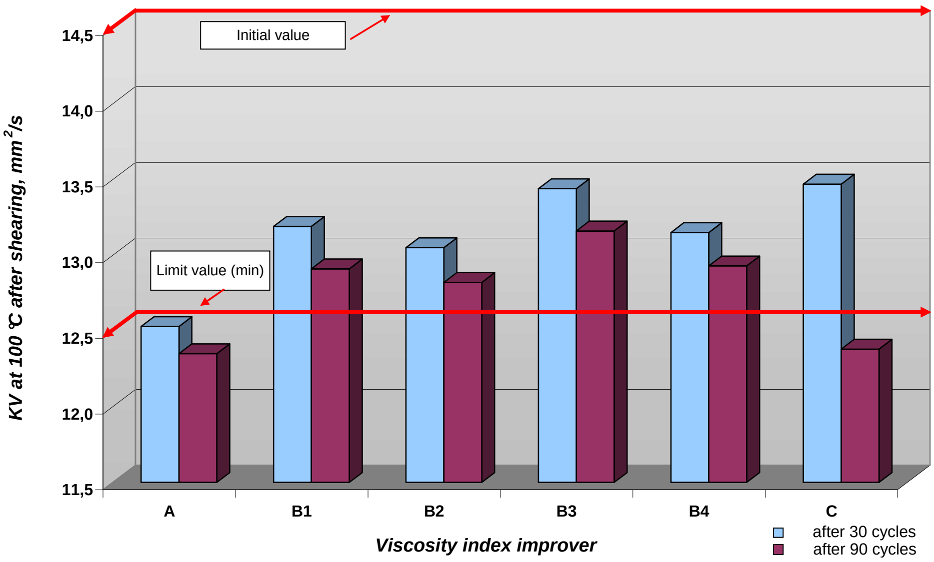
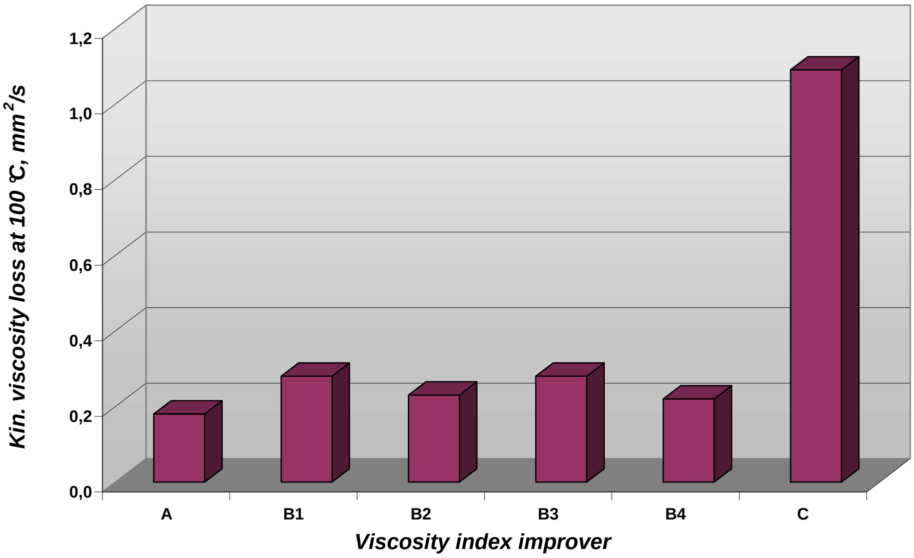


Figure 5: Kinematic viscosity loss at 100 ℃ from 30 to 90 cycles of testing



7. Conclusion

1. New international specifications ACEA and API require that the shear stability of engine oils is tested by 90 cycles of oil passing through the nozzle instead of current 30 cycles; these requirements are accepted by a number of vehicle manufacturers.
2. Shear stability determination according to new ASTM D 7109 method has been defined with 90 cycles of testing.
3. Different concentrations of viscosity index improvers are needed for production of multigrade engine oil of the same viscosity; the highest additive concentration is needed for the viscosity index improvers based on OCP.
4. Viscosity index improvers based on OCP have the best shear stability after 90 cycles of testing.
5. Engine oil with the viscosity index improver based on styrene-isoprene (C) has a significant viscosity loss after extended testing from 30 cycles to 90 cycles and it does not meet requirements of the new international and OEM specifications.

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UDK	ključne riječi	key words
665.765.038.64	poboljšivači viskoznosti	viscosity improvers
678.744.33	polialkilmetakrilatni poboljšivač indeksa viskoznosti	polyalkylmetacryilate VI improver (PAMA)
621.892.097.2	multigradno motorno ulje	multigrade motor oil
532.133.091	smična stabilnost	shear stability
.002.237	gledište pooštrenja zahtjeva	viewpoint of increasing requirement

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