Czech University of Life Sciences Prague
Technical Faculty

Technology and Environmental Engineering

Department of Technological Equipment of Buildings

Diploma Thesis

Comparison of different methods of combustion engine's cleaning

Author: Kristina Truvaleva

Supervisor: Ing. Petr Miler, Ph. D.

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II. DECLARATION

I hereby declare that I have elaborated this master thesis independently. All information sources are quoted in References.

Kristina Truvaleva.. 9th April 2011 Prague, Czech Republi

III. ABSTRACT

Nowadays, internal combustion engines and their construction have a great meaning in automobile industry. But reliable work of the engine depends not only on quality of manufacturing and assembly but also on operating rules and service.

The aim of the thesis is to analyze two main methods of Internal Combustions Engines cleaning:

- Cleaning-in-place method (with use of detergents and additives);
- Demountable method.

Cleaning-in-place method is performed by using additives (detergents, dispersants, etc.).

Automobile taken to show this method was Hyundai Elantra 2005. Equipment for measuring compression was simple compression tester; set for cleaning included Decoking LAVR ML-202 Anti Coks and Engine Wash Motor Flush. Also were taken into account results, comparisons and analysis from different sources and for better theoretical justification.

Keywords:

engine, cleaning-in-place method, demountable method, additives, engine performance, CPG of engine, exhaust gases, emissions.

ABSTRAKT

V dnešní době, spalovací motory a jejich konstrukce mají velký význam v automobilovém průmyslu. Ale spolehlivá práce motoru závisí nejen na kvalitě výroby a montáže, ale i na provozních podmínkách a údržbě.
Cílem práce je analyzovat dvě hlavní metody čištění spalovacích motorů:
- metoda čištění na místě („in-place“) (s použitím detergentů a přídatných látek);
- metoda rozebíratelná („demountable“).
Metoda čištění in-place se provádí pomocí přísad (detergenty, dispersanty atd.)
Automobil na kterém je ukazovánatatometoda je Hyundai Elantra 2005. Zařízením pro měřeníkompresebyljednoduchákompresor tester, sada pro úklidkarbonovýchusazeninLavr ML-202 Anti Coks a čističmotoru. Rovněžzdebylyvzaty v úvahuvýsledky, srovnávání a analýzy z různýchzdrojů pro lepšíteoretickézdůvodnění.

Klíčová slova:
motor, metodačištěníin-place, metodademontážní, aditiva, výkonmotoru, CPG motoru, výfukovéplyny, emise.

1. INTRODUCTION

Our motion in space in most cases occurs in a transport in motion, which drives an internal combustion engine (ICE).

From what positive engine work depend on? First of all, reliable work of the engine depends on quality of manufacturing and assembly. However even the best engine can be spoilt, by using doubtful engine oil or bad fuel, breaking the operating rules and service. Large amount of fuel burnt during the engine operation in a combustion chamber. The part of an unburned fuel slobbers into a space between the piston and the cylinder. In turn burnt oil which always is present on the cylinder' walls picks off by the piston rings. This mixture of hydrocarbons inevitably gets into the space between rings and piston grooves. Under the influence of high temperatures fuel and oil transform to more viscous and even firm tarry- coke adjournment. Harmful tarry- coke adjournment stick" piston rings, settle on the valves and pistons, breaking their working capacity. As you understand, it leads to compression falling in the cylinders, engine power dropping, bad drive, the fuel and oil over-overconsumption, increase in toxicity of the exhaust gases etc. Coking also is a principal cause of the accelerated excessive ware of piston-cylinder assembly.

At considerable adjournment of a deposit, for its removal it is necessary to remove a cylinder head. Thus it is necessary to take the measures providing safety of a gasket. Whereas the gasket sticks (burns) to a block and head surface, the head should be removed cautiously, gradually unhooking the gasket from any flat surface.

Before cleansing the deposit should be soaked with kerosene and after clean all surfaces by a scraper. Especially cautiously it is necessary to clear a deposit with the bottoms of aluminium pistons and heads not to put scratches. It is necessary completely remove particles of the cleared deposit from the head and block by a brush, and then by a rag moistened with gasoline. After that the engine should be assembled, being careful according to the rules of safety arrangements (Smith 2003). This demountable method of cleansing is very labour-consuming and long process, therefore now the increasing interest represents application of fuel cleaners and additive compounds. Their world assortment engages more than 40 types differs according to their destination, and ten thousand commodity brands.

Using of detergent additives to petrol and diesel fuels suppose some variants. Thus for cleansing of various details of the engine special preparations are issued. In some cases additives can be added in fuel directly during the fabrication. For needs of car-care centers and private automobile owners special additive compounds in small packing are issued.

Financial viability of cleaning of engine details serves one of the basic criteria for a choice of cleansing method. It is caused by various expenses for diagnosing and cleansing of details. It is known that the demountable method of cleansing contains more quantity of operations, than cleaning-in-place method. Thus, the last one also cheaper also demands less of time for realization of failure’s elimination.

Considering told above, the purpose of the given work is to examine and evaluate the two main engine cleaning methods. To obtain better understanding of engine performance and engine problems (mainly cylinder piston group deposit and engine exhaust emissions). Main fuel properties affecting engine exhaust emissions, additives for diesel and petrol fuels and their influence on environment are taken into account in this work.

This diploma work is divided in four parts, starting with a background overview about the general information about internal combustion engines, types and chemistry of lubricant additives, then materials and methods used forexperiments, the third part consist of the conducted results and their discussions with otherauthors and companies, and the last part is conclusions of the work done.

2. LITERATURE REVIEW

2.1 Internal Combustion Engine and its classification.

The IC engine is an engine in which the combustion of a fuel appears with an oxidizer in a combustion chamber. In this engine, the expansion of high-pressure gases provided by combustion directly influence on some part of the engine.

Classification of IC engines can be according to:

1. Ignition
    - Spark ignition (SI): high potential discharge between electrodes ignites air-fuel mixture in chamber encompassing spark plug;
    - Compression ignition (CI): air-fuel mixture self-ignites because of high temperature in combustion chamber due to high compression;
2. Valve location
    - Valves in head;
    - Valves in block;
3. Number of strokes
    - Two-stroke engine has every second stroke as a power;
    - Four-stroke engine has one working stroke in every four strokes;
4. Design
    - Rotary;
    - Reciprocating;
5. Number and position of cylinders
    - In-line: cylinders are one behind the other in straight line;
    - Single cylinder;
    - V-type: two inclines of cylinder at an angle 60-90^0 with each other along a crankshaft;
    - W-type: three banks of cylinders along crankshaft;
    - Radial engine: radial position of cylinders around crankshaft;
    - Opposed piston engine: combustion chamber between two pistons in every cylinder, etc;
6. Air intake
    - Naturally aspirated: no air pressure assistance;
    - Supercharged: air pressure increased with compressor moved by exhaust gases;

- Turbocharged: air pressure increased turbine-compressor moved by exhaust gases;
- Crankcase compressed: crankcase has a role of intake air compressor in two-stroke engine;

7. Fuel used
    - Petrol;
    - Diesel;
    - Alcohol (ethyl, methyl);
    - Gas (methane or natural gas);
    - Liquefied petroleum gas (LPG): propane, butylenes and etc.;
    - Dual fuel (methane and diesel);
    - Biodiesel: vegetable oils;
8. Cooling system:
    - Water cooled;
    - Air cooled;
9. Fuel input method (Stone 1999, Ganesan 2007):
    - Carbureted: air-fuel mixed at throat;

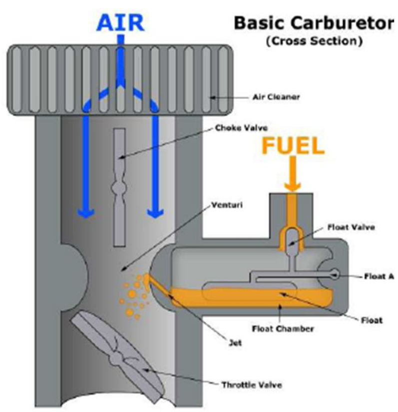


Fig. 1 Basic carburetor

- Fuel injection:
  - Throttle body fuel injection;
  - Multipoint port fuel injection;

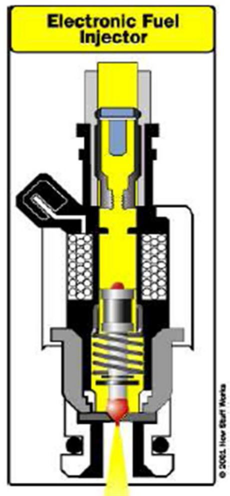


Fig. 2 Electronic fuel injector

2.2 Main components of engine:

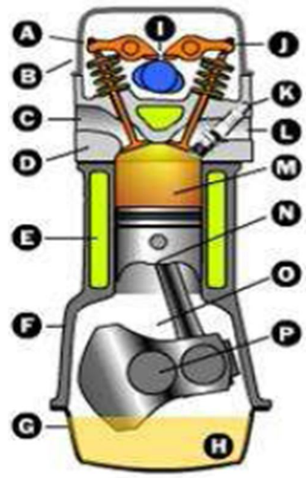


Fig. 3 Main components of engine

A- Intake valve, spring and rocker arm;
B- Valve cover;
C- Intake port;
D- Cylinder head;
E- Coolant;
F- Engine block;
G- Oil pan;
H- Oil sump;

I- Camshaft;
J- Exhaust valve, spring and rocker arm;
K- Spark plug;
L- Exhaust port;
M- Piston;
N- Connecting rod;
O- Rod bearing;
P- Crankshaft.

Internal combustion engines mainly used in the transport sector; motor cars, small ships and aircrafts and submarines. But mainly this research is based on engines used in automobiles.

There are many problems related with engines. But before fixing of these problems you have to provide general diagnosis of car. It is called maintenance.

Auto maintenance describes the act of inspecting or testing the condition of car subsystems (e.g., engine) and servicing or replacing parts and fluids. Regular maintenance is critical to ensure the safety, reliability, drivability, comfort and longevity of a car. During preventive maintenance, a number of parts are replaced to avoid major damage or for safety reasons, e.g. timing belt replacement.

The actual schedule of car maintenance varies depending on the year, make, and model of a car, its driving conditions and driver behavior. Car makers recommend the so-called extreme or the ideal service schedule based on impact parameters such as:

- number of trips and distance traveled per trip per day
- extreme hot or cold climate conditions
- mountainous, dusty or de-iced roads
- heavy stop-and-go vs. long-distance cruising
- towing a trailer or other heavy load

Experienced service advisors in dealerships and independent shops recommend schedule intervals, which are often in between the ideal or extreme service schedule. They base it on the driving conditions and behavior of the car owner or driver.

Common car maintenance tasks include:

- Car wash;
- Check/replace the engine oil and replace oil filters;
- Check/replace fuel filters;
- Inspect or replace windshield wipers;
- Check or refill windshield washer fluid;
- Inspect tires for pressure and wear;
- Tire balancing;
- Tire rotation;
- Wheel alignment;
- Check, clean or replace battery terminals and top up battery fluid;
- Inspect or replace brake pads;
- Check or flush brake fluid;

- Check or flush transmission fluid;
- Check or flush power steering fluid;
- Check and flush engine coolant;
- Inspect or replace spark plugs;
- Inspect or replace air filter;
- Inspect or replace timing belt and other belts;
- Lubricate locks, latches, hinges;
- Check all lights;
- Tighten chassis nuts and bolts;
- Check if rubber boots are cracked and need replacement;
- Test electronics, e.g., Anti-lock braking system or ABS;
- Read fault codes from the Engine control unit.

Some tasks that have equivalent service intervals are combined into one single service known as a tune-up. In modern cars, where electronics control most of the car's functions, the traditional tune-up doesn't apply anymore. Maintenance jobs like a tune-up used to mean getting the engine's performance back on track. Today embedded software takes care of it by constantly checking thousands of sensor signals, compensating for worn-out spark plugs, clogged filters, etc. The so-called limp-home function allows driving on limited power when the engine is in trouble. In the old days this might have meant a breakdown.

Here I am going to focus on engines cleaning and there are two maincleaning methods:

- demountable (divisible) method of cleaning;
- cleaning-in-place (indivisible) method of cleaning.

2.3 Engine cleaning methods

2.3.1 Demountable method of cleaning

During continuous operation of engine there is a layer of soot on the walls of the combustion chamber, valves and piston bottom. The soot is formed from particles of no completely burned fuel and oil, which penetrates into the cylinder from the crankcase, as well as from dust that fall into the cylinder with air. The carbon deposition becomes faster in case of poor air cleaning, insufficient fuel feed system performance, and entry of the oil into the combustion chamber due to significant wear of rings, pistons and cylinders. To remove small amount of soot deposit without disassembly of the engine it is necessary to add kerosine oil into cylinders of the warmed-up engine and keep it for the whole night. The next day, after scavenging the cylinder and changing of the oil in the crankcase it is useful to give the engine run with increased speed and good warming-up. Long-term forced engine working on load along with good warming-up is also used to remove soot. For example, by mileage at the rate 60-80 km/hour, for 1-2 hours. At the same time can be cylinders self-cleaning from the soot as a result of its burning. If there is significant amount of soot deposit it is required to remove the cylinder head. It is necessary to assume measures to ensure the safety of cylinder ring. Because the ring sticks (burns) to the surface of the block and head, the head must be removed carefully, slowly separates ring from the plane surface. Before cleaning the soot deposit should be soak in kerosene oil and then removed from all surfaces with a scraper. You have to pay strict attention in removing soot from the bottom of the aluminum pistons and heads, not to cause scratches. Particles of scavenged soot must be removed from the head and block with a brush, and then with a rag soaked with gasoline. After that, the engine must be assembled in accordance with safety standards.

2.3.2 Cleaning-in place method

One of the main reasons of low quality of vehicles is the unsatisfactory manufacture and insufficient level of maintenance and repair. Most of the population is not adequately informed about the possibilities of an effective impact on its quality through changes of operating conditions, using the latest achievements in the field of tribology, such as: modern lubricants, special tools and technologies developed by leading hydrocarbon processing firms etc. Cleaning-in-place technology is more versatile. In recent years a growing interest presented in special compositions which are focused on modifying the tribological performances of surfaces in friction units of machines, primarily to reduce traction coefficient and wear.

2.3.3 Cleaning-in-place method for diesel engine

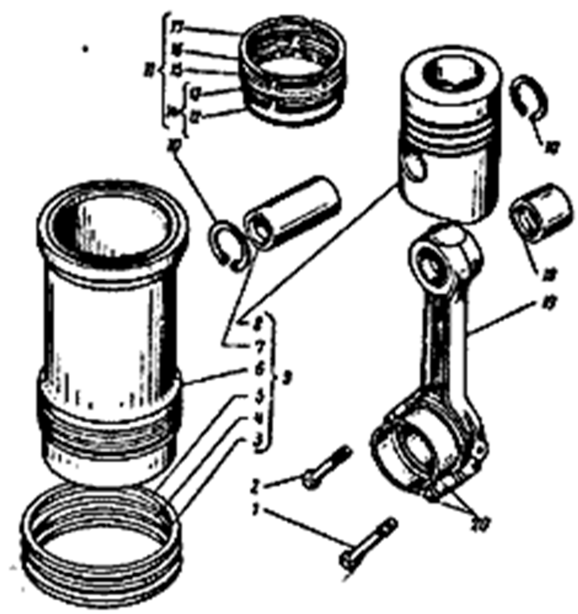


Fig.4 Cylinder piston group of diesel engine

During diagnosis of CPG details it is necessary to ensure in operability of other units and engine systems. For example, in case of increased oil consumption in the topping (above1.5%) it is necessary to provide no oil leakage from engine and depressurization of the inlet system. Diagnosis before engine disassembly should be started with determining of the conditions of the engine and quality and volume of corrective maintenances and maintenance operations performed. Under conditions of running it is necessary to evaluate engine's loading according to fuel consumption in l/100 km (l/machine hour), and heating rate, noise or knocking during engine operation. It is also necessary to identify possible motor stoppage. After performing above mentioned operations if it is possible start the engine and listen to its operating under no-load conditions on idling from minimum to maximum speed of the crankshaft. You have to inspect deposits from paper element of oil filter and from spin oil filter. Turn special attention to the amount of deposit and the presence of metal shavings.

There are 2 methods:

1. To sample oil from the crankcase in amount of 250-500 ml and submit it to the chemical laboratory for physicochemical parameters of oil (viscosity, base number, the amount of insoluble residue, the presence of water in the oil, dispersant properties, etc.);
2. Or can be used methods of instrumental diagnosis. This way, we measure engine cylinders pressure at the end of the compression stroke. It is defined in absolute units with compressometer.

Compressometer measured compression pressure due to scrolling crankshaft with a starter or due to the engine running at a minimum idle frequency. The compression pressure magnitude if rpm =800 min^{-1} must be Rc=3.0−3.5MPa (30−35 kg/cm2). Particular attention should be paid on the pressure difference Pc in the cylinders. This comparison will help to determine cylinder with defective parts of the CPG.

According to the values of Pc we can determine following defects of CPG component parts: piston burnout, compression ring fracture, component parts wear, piston ring sticking, scoring of rings and valve float .In these cases value of Pc in the cylinder usually less than 2.0−2.1 MPa (20−21 kg/cm2).

Tab.1 Defects of CPG component parts and their causes

Defects	Possible causes	Annotation
Compression ring fracture	Oil retreat or using of oils which are inconsistent with service instructions	-
Oil-control ring wear	Motor oil low quality	Requires inspection of the oil filter parts and of the non-return valve
Increased wear of rings, grooves and sleeves	Air filtration low quality	Check the condition of the air cleaner elements and leakproofness of car or tractor intake system

2.4 Additives to diesel fuel

Additives can strengthen various diesel fuel properties. For example, to increase the cetanenumber of the fuel usually used ignition improver additives. Detergent additives mainly aimed for controlling the formation of fuel deposits that can have detrimental effects on combustion. The build-up of lacquer and carbonaceous deposits on injector tips can affect the amount of fuel injected and the spray pattern, and be the reason of reduced power and higher smoke emission. The cold flow performance of diesel fuel can be adjusted to prevailing climatic conditions by base component selection, but at the expense of cetane quality and an availability penalty. Nonetheless, by using cold flow additives, the required low-temperature filterability can be obtained at nearly constant cetane number.

Diesel fuel additives have a great influence on improvement of quality of diesel fuels towards to noise, emissions, engine performance, and customer perception, while offering flexibility in the optimization of refinery production costs.

There are different ways to classify diesel additives, in the following, they are divided into two classes:

1. Additives influencing diesel fuel combustion: combustion improvers, ignition improvers, catalysts for regeneration of after treatment devices, and detergents.
2. Additives influencing storage and flow (dehazers, anticorrosion, antioxidants, antifoam, antirust, biocides, additives for low-temperature operability, etc.) (Sher 1997).

2.5 Chemistry of lubricant additives

2.5.1 History of additives development

“Until the 1930s crankcase engine oils contained no additives, comprising only base oils. Oil drain intervals were necessarily very short (1,500 km or less) to ensure adequate lubrication. The existing oil classification system, first adopted in America in 1911 by SAE (American Society of Automotive Engineers) was related only to oil viscosity and not performance.

The main steps of lubricant additive development - 1930s to the present:

Fig. 5 gives a chronological view of the development of the main additive families. These developments have been driven by new specification demands imposed by engine design changes, which in turn are a response to consumer demand and emissions requirements.

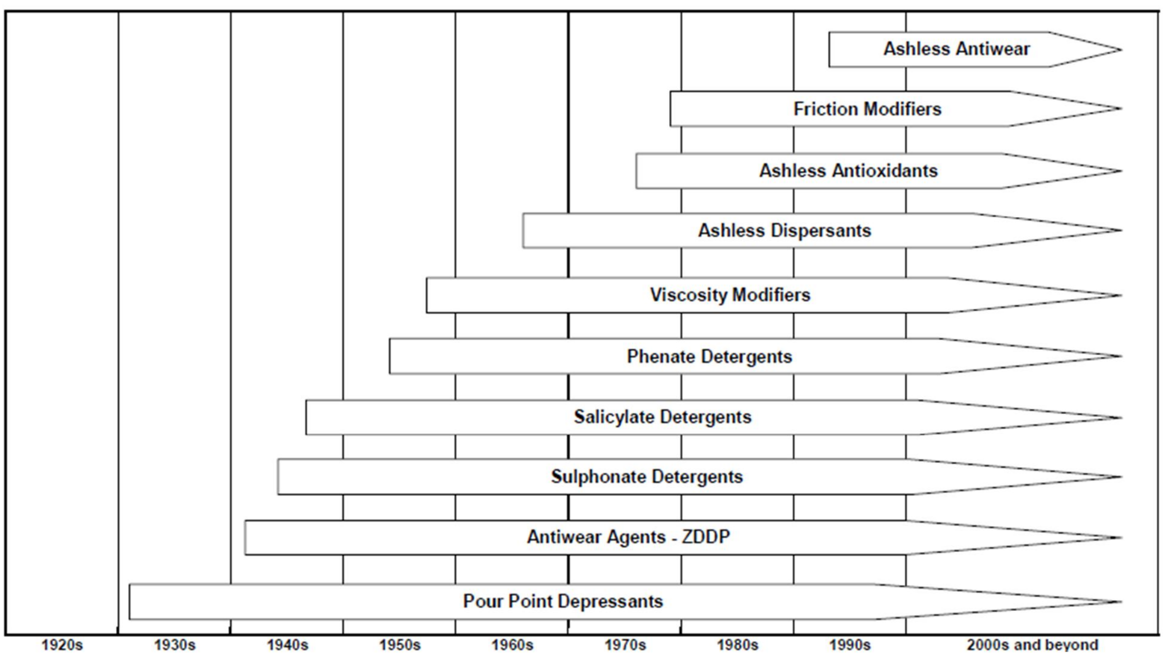


Fig. 5 Development of lubricant additives

2.5.2 Main additive component families

- Pour point depressants (1932)
- Zinc dialkyldithiophosphates (ZDDP) antioxidant /antiwear agents (1940)
- Detergent sulphonates and salicylates (1940s)
- Detergent phenates (1950s)
- Polymeric viscosity modifiers (1950s)
- Ashless dispersants (1960s)
- Inhibitors (1970s)
- Friction modifiers (1970s)
- Ashlessantiwear (1990s)

Future development is driven by evolution in engine design to meet more stringent emissions legislation and increasing consumer demands" (quoted from ATC Document 49,2007).

Lubricant additives can be divided into two categories:

- those protecting engine' metal surfaces (for example, antiwear, anti-rust, anticorrosion and friction modifier additives);
- those buttressing base stock performance (for example, dispersants, viscosity modifiers, antioxidants, and pour point depressants).

Detergent additives have role in both areas.

2.5.3 Oil soluble materials

Main parts of additives are oil soluble materials. In fact, many are prepared using oil as a solvent. For better storage stability and handling reasons, many additives are made as 45 - 90 wt. % concentrates of active material in oil. "Polymeric additives used as viscosity modifiers can be diluted even more to facilitate handling. Additive molecules typically have long, oil soluble, hydrocarbon (non-polar) tails and smaller, hydrophilic (polar) head groups (Fig. 6). Since the two parts of the molecule have different solubilities in oil, additives therefore tend to exist colloidally as inverse micelles (Totten, 2003).

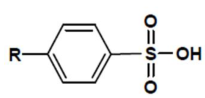
Fig. 6 Schematic representation of a polar additive molecule

2.5.4 Detergents

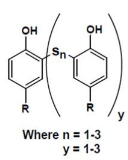
Oil-soluble detergents are formed by combining a polar substrate with a metal oxide or hydroxide. The polar substrate is made up of two parts. The hydrocarbon tail or oleophilic group acts as the solubiliser enabling the detergent to be fully compatible and soluble in the base stock. The polar head contains the acidic group which reacts with the basic metal oxides or hydroxides" (quoted from quoted from ATC Document 49,2007) .

Detergent polar substrates types fall into three main classes:

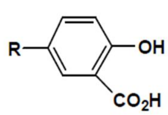
- Sulphonates



- Phenates



- Salicylates



Moreover some metals have been includedd into detergents, only two metal cations are now commonly used – calcium and magnesium.

"The detergent can be neutral, where the salts are simple and contain roughly stoichiometric amounts of the metal and polar substrate (Fig.7). It is possible, however, to incorporate large amounts of metal base (for example calcium carbonate) by blowing carbon dioxide through a reaction mixture containing excess metal oxide or metal hydroxide, producing an overbased detergent (Fig. 8).

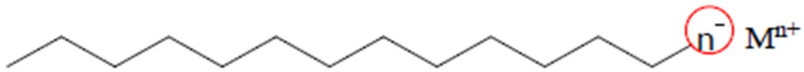


Fig. 7 Neutral detergent

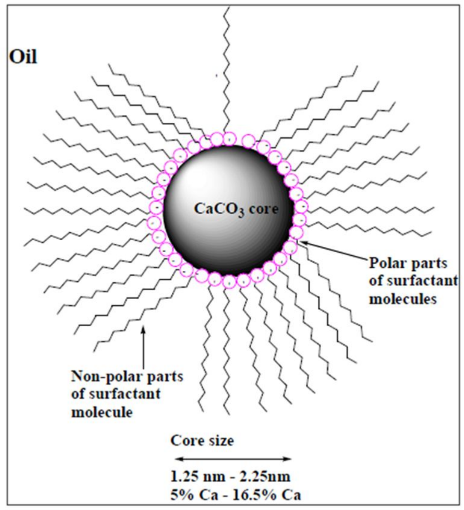


Fig. 8 Overbased detergent

The overbasing level is indicated by the Base Number (BN), measured using potentiometric titration which expresses the basicity of the detergent in terms of the equivalent number of milligrams of potassium hydroxide per gram of detergent" (quoted from quoted from ATC Document 49,2007).

Mode of action:

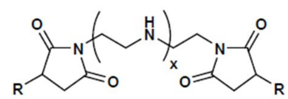
Detergents reduce soot formation and provide anticorrosion and antirust protection. Deposit precursors, being oil insoluble, have a greater affinity for detergent molecules than oil molecules. They are attracted to detergent micelles and trapped within them. Therefore, they are locked in the oil solution and cannot settle out to form deposits in the engine. On particles of less than 20nm diameter, the detergents form adsorbed films surrounding the particle surface, which slow down coagulation. Larger particles (50 – 150nm) usually have an electrically charged surface that can attract the detergent substrate that forms a stabilizing layer thus preventing particle agglomeration (McCaleb 1990).
Some detergentsalso may have a role of antioxidants.

2.5.5 Dispersants

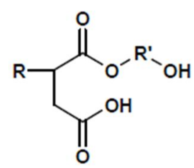
“Dispersants consist of a polar head, the polarity of which is derived from oxygen or nitrogen moieties, and a hydrocarbon or oleophilic tail, typically poly isobutene, which enables the substrate to be fully oil soluble. They are generally referred to as ashless, containing no metal to form ash on combustion, but can also contain small amounts of boron derived from boric acid which is sometimes used as a capping agent.

Three main types of ashless dispersant are in use:

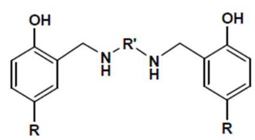
- Succinimides



- Succinic esters of polyols

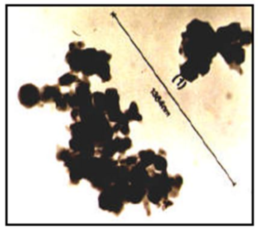


- Mannich bases

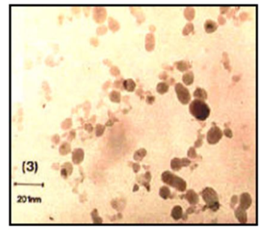


Ashless dispersants have longer hydrocarbon tails than the detergents but function similarly in that they form micelles that trap deposit precursors such as soot or sludge. Particles up to about 50nm (cf. 20nm for detergents) can be stabilised by the thicker adsorbed film. Dispersants that contain an ionisable polar head (for example succinimides) can also stabilise larger particles by charge repulsion. An ashless dispersant micelle can attract and hold at least ten times more sludge particles than a detergent micelle. Their effectiveness is shown in Fig. 9. Ashless dispersants are also highly effective at stabilising soot produced by diesel engines, preventing particle agglomeration and hence oil thickening.

Dispersant viscosity modifiers are ashless too, but have a higher molecular weight. They form even thicker barrier films by attaching themselves to particles at several points and can stabilise particles up to about 100nm" (quoted from Rudnick, 2003).



Poor dispersancy



Good dispersancy

Fig. 9 Dispersion by dispersants

2.5.6 Inhibitors

Inhibitors are used to minimiseand reduce wear, corrosion, oxidation, foam, friction andrust. The main chemical families are zinc dithiophosphates (ZDDPs), hindered phenols, phosphorus compounds, aromatic amines, polysiloxanes and sulphurised fatty acid derivatives. ZDDP additives can be divided into primary alkyl and secondary alkyl ZDDPs. Different ZDDP chemical types perform differently (Tab. 2). Each type has its important role in additive packages. The choice of the alcohols used in the preparation of the ZDDP ascertains effectiveness of the ZDDP as an anti-wear agent but also its ability to confront the heat and water effects i.e. thermal and hydrolytic stability (ATC Document 49,2007).

Tab. 2 Performance parameters of different ZDDP types

	Primary Alkyl	**Secondary Alkyl**
Thermal Stability	Medium	Low
Antiwear Protection	Medium	High
Hydrolytic Stability	Medium	High

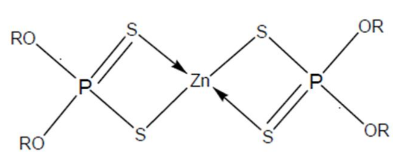


Fig. 10 The general structure of a ZDDP (Zinc dialkyldithiophosphates)

2.5.7 Antiwear

"Hydrodynamic lubrication is maintained by a multimolecular film of lubricant between the surfaces involved. There is no wear without contact of surfaces. Nonetheless, hydrodynamic lubrication is not always possible. If loads are high, or viscosity of lubricant is too low, surface asperities on the moving parts make contact (Fig. 11). This contact between the lubricated surfaces is named boundary lubrication. Under these conditions, reduction in friction is achieved through the antiwear additive adhesion to the metal surface and the formation of a lubricating solid film" (quoted form ATC Document 49, 2007).

Most anti-wear agents work by forming low shear films on metal surfaces. ZDDPs are notably the most effective multifunctional types.

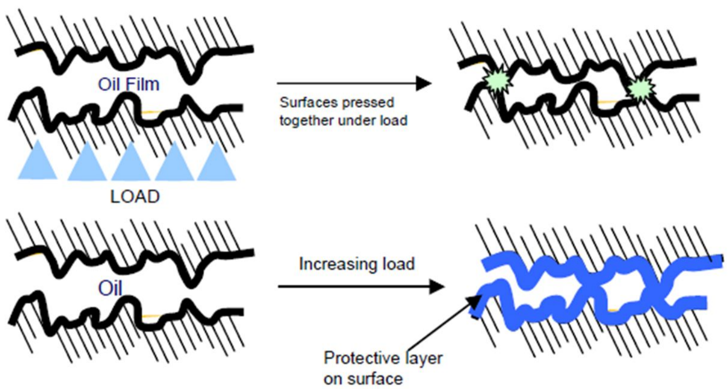


Fig. 11 Illustration of boundary lubrication

The mode of action of phosphorus additives is similar to that of ZDDP. Mainrole is reduction of friction during boundary lubricationthrough the adhesion of the additive or its thermal division product to the metal surface layers (ATC Document 49, 2007; Rudnick 2003).

2.5.8 Antioxidancy and anticorrosion

Oxidation of an oil leads to the oil darkening and thickening as chemical species are broken down forming insoluble sludge or soot particles. Organic acids are produced which are extremely corrosive towards non-ferrous metals leading, for example, tobearing corrosion. Further oxidation leads to the build up of polymeric material. This high molecular weight oxygenated polymers cause oil thickening as well as varnish and gum deposits on pistons and other engine components.

Inhibitors work as antioxidants by disrupting the chain propagating steps of the oxidative process by which these insoluble species are formed (Fig. 12). The oxidative process is a chain reaction that once started and left unchecked increases at an exponential rate producing increasing amounts of free radical and or peroxide species. The inhibitors themselves function as either peroxide decomposers or as free radical traps.

ZDDPs are able to act as antioxidants by disrupting the chain propagation steps of the oxidative reaction, by acting as either peroxide decomposers or free radical traps. ZDDPs also act as metal deactivators or anticorrosion agents by forming protective films on metal surfaces.

Initiation:	$RH \rightarrow R^{\bullet}$
Propagation:	$R^{\bullet} + O_2 \rightarrow ROO^{\bullet}$
	$ROO^{\bullet} + RH \rightarrow ROOH + R^{\bullet}$
	$ROOH \rightarrow RO^{\bullet} + HO^{\bullet}$
	$RO^{\bullet} + RH \rightarrow ROH + R^{\bullet}$
	$HO^{\bullet} + RH \rightarrow R^{\bullet} + H_2O$
Termination:	$R^{\bullet} + ROO^{\bullet} \rightarrow ROOR$
	$R^{\bullet} + R^{\bullet} \rightarrow R\text{-}R$

Fig. 12 Oxidation chain reaction

Hindered alkyl phenols intercept deleterious free radicals to form stable hindered radicals that are not prone to propagation (Fig. 13). These free radical traps help maintain the viscosity characteristics and long term performance of the lubricant, limiting damage to the viscosity modifiers, and reducing lacquer formation from the base oil.

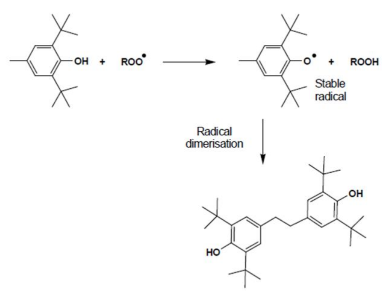


Fig. 13 Radical trapping by hindered phenols

Aromatic amines have a complementary mode of action to that of the phenolic family (Rasberger 1997, Totten 2003).

2.5.9 Friction Modifiers

Power loss from friction in internal combustion engines is derived from the viscous drag of the lubricant and friction losses through heat generation under mixed and boundary lubrication conditions. The former can be reduced by decreasing the viscosity of the oil, but only to the point where a lubricant film is maintained, which keeps moving parts separated.

Boundary lubrication occurs in various stressed parts of the engine, for example between rings and liners at the top of the piston travel and in the valve train between cam and lifters etc. In this type of lubrication the oil film is not adequate to keep moving parts separated and this function is taken over by a film of polar molecules strongly absorbed on the metal surface. The drag caused by this boundary lubrication depends on how easily these surfaces slide past one another. One way to reduce the energy losses and maintain a boundary film is by using friction modifiers.

By definition, the base fluid itself is the primary friction modifier, but the need for fuel economy has required additional friction modifiers. Friction modifiers are closely related to antiwear additives in mode of action. They are generally straight hydrocarbon chains with a polar head group.

Typical polar head groups are:

- Amines, amides and their derivatives
- Carboxylic acids or derivatives
- Phosphoric or phosphonic acids and their derivatives.

Molybdenum compounds such as molybdenum dithiocarbamates, molybdenum dithiophosphates and other more complex molybdenum compounds are extensively used for friction modification. These compounds react on the metal surface to yield molybdenum disulphide that has a structure that allows sliding and shearing to take place (ATC Document 49 2007, Totten 2003).

Examples of common friction modifier types are (their treating dosages range from 0.1 to 1.5% and chemical types include):

- Sulphurised fats and esters
- Amides of fatty acids
- Polyol esters of fatty acids e.g. glycerylmonooleate (GMO, Fig. 14)
- Molybdenum compounds e.g. molybdenum dithiocarbamate (MoDTC, Fig. 14)

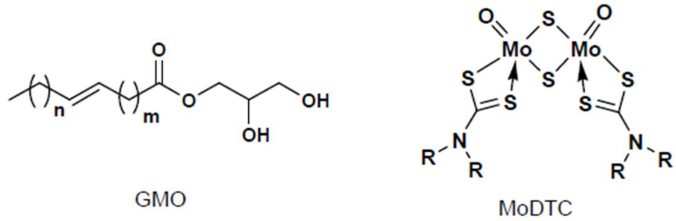


Fig. 14 Friction modifiers

2.5.10 Antifoam Agents

The presence of additives can slow up the release of gases churned into lubricating oil. This may result in foaming and/or air entrainment. Air entrainment, especially in modern, high speed, high temperature engines, may result in diminished engine reliability.

Foam is countered by adding tiny amounts of antifoam additives. Silicon chemicals, such as polydimethylsiloxanes (Fig. 15) are very commonly used as antifoam agents.

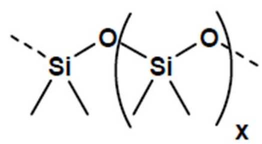


Fig. 15 Polymethylsiloxane antifoam

Since these materials are not very oil soluble, they separate from the oil onto the surface of air bubbles and cause them to rupture by reducing the surface tension. Common treating dosages for such antifoams are between 10 to 100 ppm in oil. Polyacrylates are particularly effective air release agents.

2.5.11 Viscosity modifiers

By suitable formulation, it is possible to make an engine lubricant that satisfies both the low and high temperature requirements of the SAE Viscosity Classification System, J300. This entails meeting, simultaneously, the limits for low-temperature Wgrades (determined with a Cold Cranking Simulator (CCS) and Mini Rotary Viscometer (MRV)) and high-temperature grades (kinematic viscosity at 100°C). High molecular weight polymers, known as viscosity modifiers or viscosity index improvers are commonly used for this purpose. Such oils are referred to as multigrade oils (e.g. SAE l0W40). Their viscosity is less sensitive to temperature than that of monograde oils having the same high temperature viscosity (e.g. SAE 40). As a consequence, multigrade oils allow acceptable engine operation over a much wider temperature range. Multigrade oils have a lower viscosity at low temperatures allowing easier cranking and starting than the corresponding monograde oil and as a result improved fuel consumption. These effects are shown schematically in Fig. 16 (ACT Document 49, 2007).

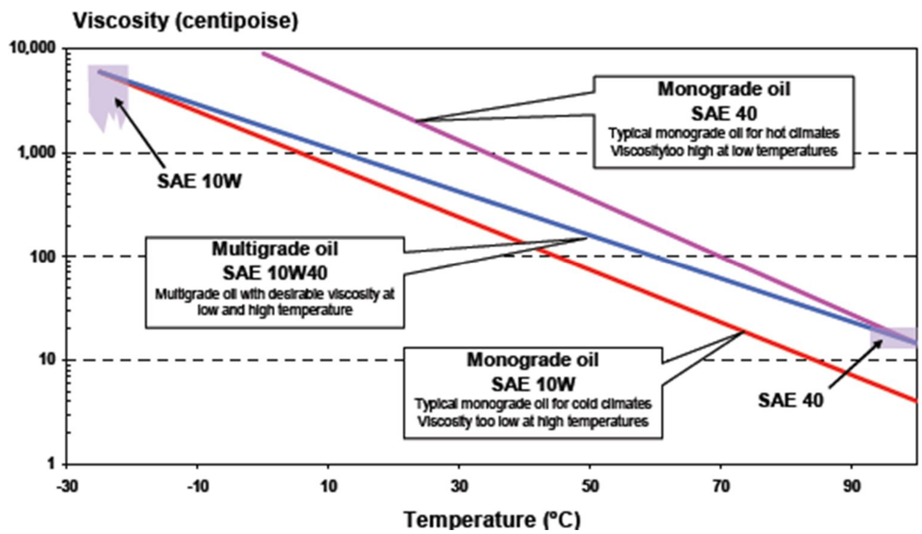
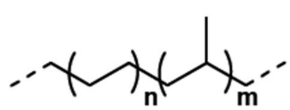
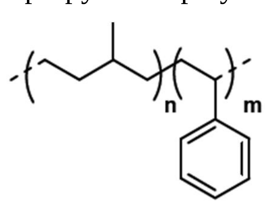


Fig. 16 Effects of temperature on viscosity

Higher molecular weight polymers (from 50,000 to 500,000) of various chemical types are used as viscosity modifiers for multigrade lubricants. The main chemical families are olefin copolymers, hydrogenated styrene-diene copolymers (Fig. 17) and polyalkylmethacrylates.



Ethylene-propylene copolymer (OCP)



Hydrogenated styrene isoprene copolymer

Fig. 17 Viscosity modifiers

For ease of application, viscosity modifiers are generally diluted in low viscosity base oil to a concentration of between 5 and 50 % mass depending on the solubility and the viscosity of the polymer. The function of the viscosity modifiers is to decrease the slope of the viscosity /temperature relationship. In addition to their ability to modify oil viscosity, viscosity modifiers can provide other functions such as dispersancy. Some dispersant viscosity modifiers exhibit excellent soot handling and improved wear control, the latter being due to a reduction in abrasive wear (ATC Document 49, 2007).

2.6 Additives and Environment

The biosphere is the global sum of all ecosystems. It can also be called the zone of life on Earth, a closed (apart from solar and cosmic radiation) and self-regulating system.

Its pollution can directly affect on human health and living organisms. Others are fraught with indirect effects, for example, carbon dioxide emissions affect the climate, which in turn affects food production, changes in the concentrations of biogenes leading to a loss of some populations and the rapid parturition of others.

Further I am going to provide a comparative analysis of quantitative and qualitative characteristics of the emission under demountable and cleaning-in-place methods of engine's cylinder-piston group.

To solve this problem we will go through the following questions:

- Harmful effects of certain components of exhaust gases on the human body;
- The chemical constitution and the amount of harmful substances emitted into the atmosphere without use of detergents or fuel additives;
- Ways of emissions and toxicity reduction;
- Review of detergents and fuel additives.

Since the 1950s it became clear that automobile emissions are the main source of urban air pollution. It is the main source of carbon monoxide (CO) and of lead. Light trucks, heavy trucks, and off-road vehicles also contribute significantly (Sher 1998).

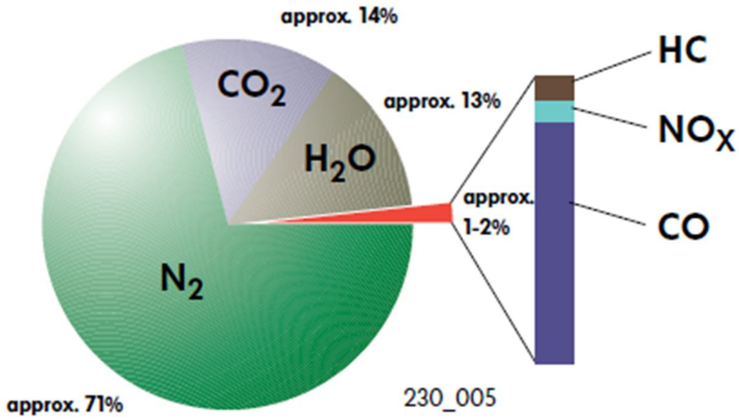


Fig. 18 Composition of exhaust emissions of petrol engines
(Audi, Self - Study Programme 230, 2000)

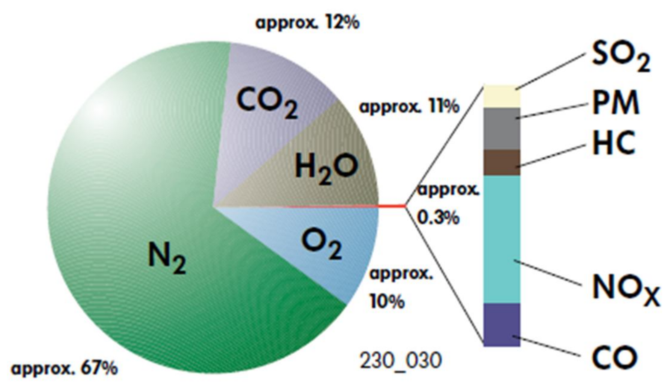


Fig.19 Composition of exhaust emissions of diesel engines

(Audi, Self - Study Programme 230, 2000)

Tab. 3 Composition of automobile Exhaust gases

Combustion-engine exhaust gases *All figures are approximate*			
Petrol		**Diesel**	
Compound	**% of total**	**Compound**	**% of total**
N_2	71	N_2	67
CO_2	14	CO_2	12
H_20	13	H_20	11
CO	1 - 2	O_2	10
Trace elements	< 0.5		~ 0.3
NO_x	< 0.25	NO_x	< 0.15
C_xH_y	< 0.25	CO	< 0.045
SO_2	possible traces	PM	< 0.045
		C_xH_y	< 0.03
		SO_2	< 0.03

- N_2 = Nitrogen
- CO_2 = Carbon dioxide
- H_20 = Water
- O_2 = Oxygen
- C_xH_y (or H_x or HC) = Hydrocarbons
- CO = Carbon Monoxide
- NO_x = Nitrogen oxides
- SO_2 = Sulphur dioxide
- PM = Particulate matter

The following diagram shows a summary of the intake and exhaust components of the combustion cyclewhich takes place in the engine **(**Audi, Self - Study Programme 230, 2000)**.**

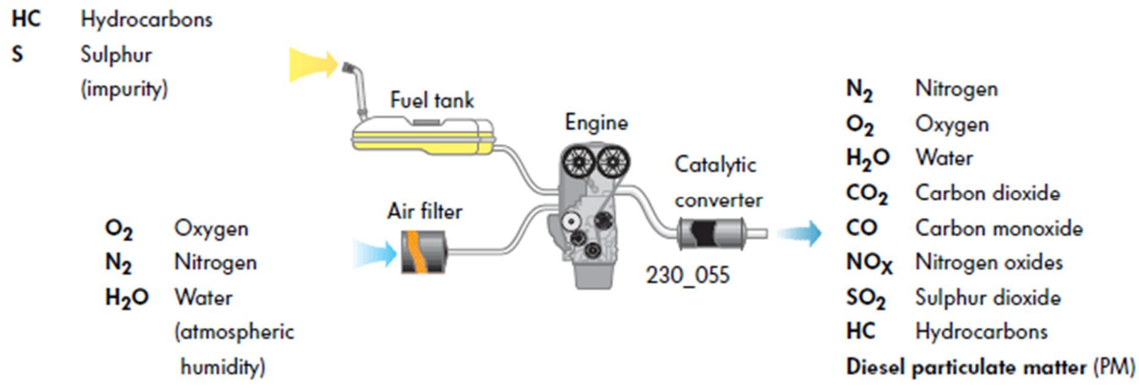


Fig.20 summary of the intake and exhaust components of the combustion cycle in the engine

In Europe, cars, trucks, and off-road vehicles are responsible for about 40% to 50 % of the HC or VOC emissions, 50 % of the NOx emissions, and 80 % to 90 % of the CO emissions in urban areas.

Significant amount of these emissions still comes from cars and light trucks with spark-ignition engines, nonetheless the relative influence of NOx and particulates from diesel engines is rising.

In spite of the fact that diesel trucks are an important contributor to air pollution, and diesel cars still increasing in sales in Europe due to high fuel prices and their higher efficiency, the internal-combustion engine still dominates the motor vehicle emissions problem.

All pollution emissions problems have two main directions: technical engineering issues for controlling pollution and policy/incentive issues.

Emissions can be reduced through the further methods:

1. Fuel switching and alternative fuels;
2. Exhaust-emission controls;
3. Reduced vehicle use per capita;
4. Reducing fuel consumption per distance traveled (Sher 1997).

2.6.1 Fuel economy

Main issue for vehicle systems design and lubrication is to aggrandize fuel economy, the object being to conserve resources and reduce vehicle contributions to emissions. Road transport contributes 14% of greenhouse gas emissions (Stern, 2006). The initial approach in the USA has been on Corporate Average Fuel Economy (CAFE) requirements for passenger car vehicle production.”ACEA has reached a voluntary agreement with the European Commission to reduce CO2 emissions to a target of 140g CO2/km by 2008, and a further reduction to 120g CO2/km is envisaged for 2012 (Fig. 21)”(quoted from ATC Document 49, 2007). Moreover fuel consumption control demands and demands reduce operating costs and to increase vehicle performance have resulted in fuel economy enhancements from the lubricant. European and US lubricant testing pay a significant attention on fuel economy performance. Some OEMs have introduced fuel economy requirements in specification, based on the CEC M111 fuel economy test andsome other tests (CEC document). These requirements you can see in Tab. 4.

Average CO_2 emissions of the European new car fleet

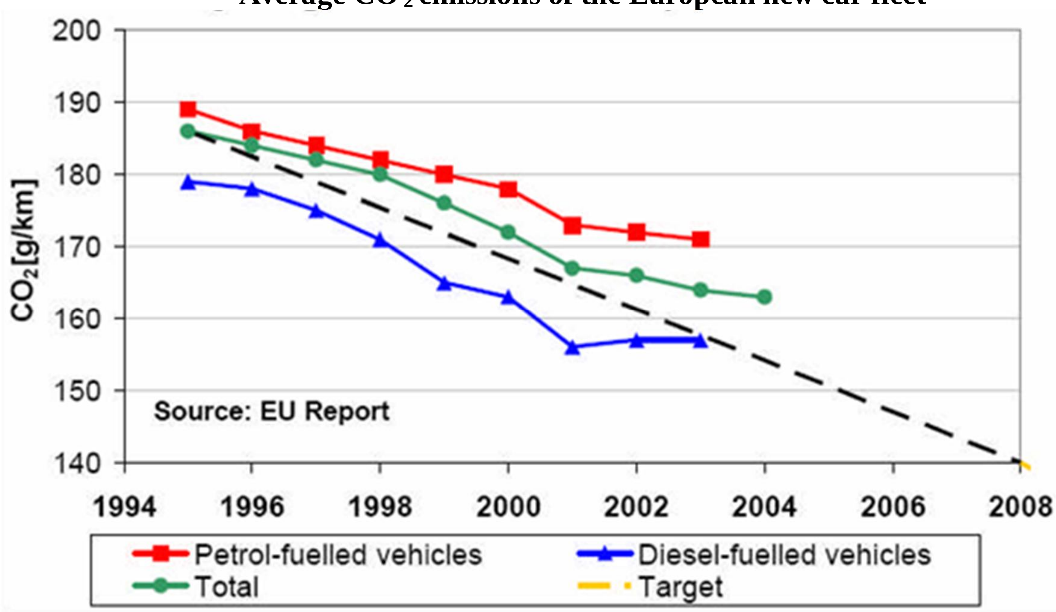


Fig. 21 Fuel economy requirements

Tab. 4 FE requirements, industry and OEM

FE requirement in CEC L-54 (M111E) test, industry and OEM	
Specification	**FE requirement**
ACEA A1/B1, A5/B5, C1	2.5%
ACEA C3	1.0%
BMW*	1.0%
Daimler	1.0 or 1.7%
Ford	2.5 or 3.0%
Opel*	1.5%
Renault	1.0%
VAG*	2.0%
* OEM test method	

Lubricant additives have a great role in fuel economy. The viscosity modifier reduces viscous drag in engine operation and increasing efficiency. Dispersants maintain system cleanliness. Friction modifiers reduce energy loss due to engine friction. Antioxidants control lubricant viscosity. Antioxidants with detergents and dispersants help retain vehicle fuel economy characteristics (ATC Document 49, 2007).

To provide some overviewon past and present emissions levels, Tab. 5 shows us typical numbers for the fuel consumed, the engine emissions, and car exhaust emissions to the atmosphere per average mile of travel. Exhaust gasesunburned carbon-containing compounds are fuel HCs and partial oxidation products that avoid burning during the normal combustion events that occur in each cylinder of the engine. Carbon monoxide emissions mainly appear when the engine is operated under fuel-rich conditions. It occurs when the air from the fuel-air mixture is insufficient to convert all the fuel carbon to CO_2. Rich mixtures give the highest possible power from the engine and help with combustion stability during engine warm-up and, in older cars, at idle (Sher 1998).

Tab. 5 Typical Automobile Fuel Consumption and Emissions

	HC*	CO grams/average mile	NO_x
Precontrol (1960s)	11	85	4
Currentvehicle: Engineemissions	3	15	2
Tailpipeemissions	0.3	2	0.4

*Fuel consumption: 120 g/mile.

The origin of no evaporative emissions from spark-ignition engines is shown schematically in Fig. 22 Sunburned hydrocarbons are produced primarily around bulk gases (cold regions where the flame does not distribute). In its turn, nitric oxides and carbon monoxide are formed via oxidation of molecular nitrogen and fuel in the bulk gases.

Nitric oxide (NO) is formed during combustion as the high flame temperatures break down molecular oxygen and nitrogen from the inducted air, which then recombine into NO. As we can see, the production of NO depends primarily on the peak temperatures that achieve during combustion process.

Carbon monoxide (CO) results from the incomplete oxidation of the fuel to carbon dioxide. Carbon monoxide formation increases as air-fuel ratio decreases and not enough oxygen is available to completely oxidize the mixture (Sher 1998).

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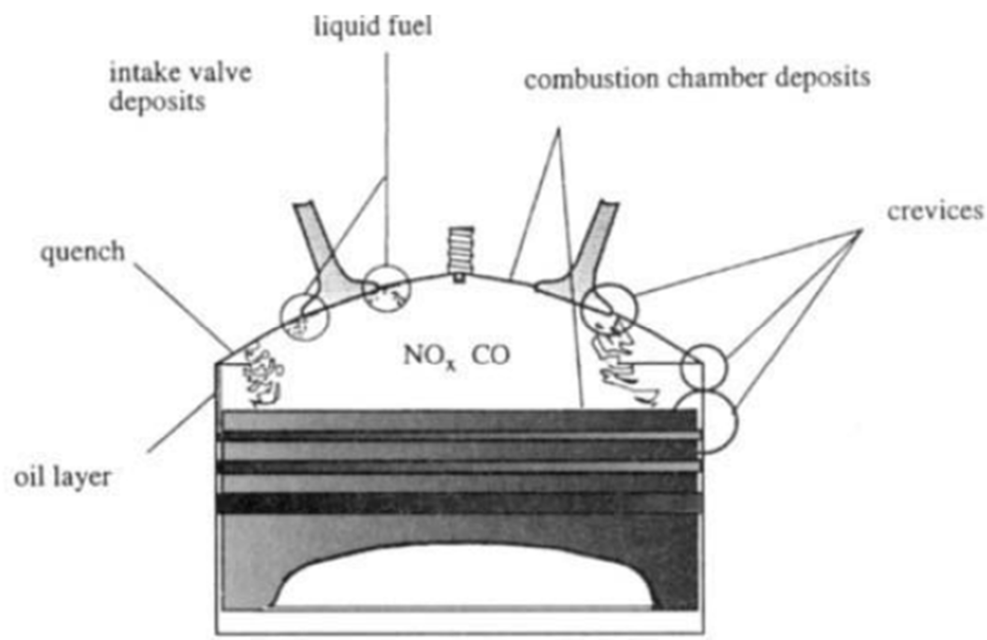


Fig. 22 Sources of pollutant formation in spark-ignited engines

2.6.2 European emission standards

Emissions standards are permanently evolving throughout the world. They reflect on for air quality requirements as well as expectations on the minimum technically feasible emission levels (Sher 1998).

For most vehicle types, including trains, cars, lorries, tractors and other machinery excluding seagoing ships and airplanes regulated emissions of nitrogen oxides (NO_x), total hydrocarbon (THC), non-methane hydrocarbons (NMHC), carbon monoxide (CO) and particulate matter (PM). For each vehicle type, different standards apply.

Emission standards for passenger cars and light commercial vehicles are encapsulated in the following tables Tab.6 and Tab. 7. Since the Euro 2 stage, EU regulations introduce different emission limits for diesel and petrol vehicles. Diesels are allowed higher NO_x emissions even in spite they have more stringent CO standards. Petrol-powered vehicles are exempted fromparticulate matter (PM) standards through to the Euro 4 stage, but vehicles with direct injection engines will be subject to a limit of 0.005 g/km for Euro 5 and Euro 6. A particulate number standard (PN) is part of Euro 5 and 6 (EC Journal, 2007).

Tab. 6 European emission standards for passenger cars (Category M*), g/km

Tier	Date	CO	THC	NMHC	NOx	HC+NOx	PM	P***
Diesel								
Euro 1†	July 1992	2.72 (3.16)	-	-	-	0.97 (1.13)	0.14 (0.18)	-
Euro 2	January 1996	1.0	-	-	-	0.7	0.08	-
Euro 3	January 2000	0.64	-	-	0.50	0.56	0.05	-
Euro 4	January 2005	0.50	-	-	0.25	0.30	0.025	-
Euro 5	September 2009	0.500	-	-	0.180	0.230	0.005	-
Euro 6	September	0.500	-	-	0.080	0.170	0.005	-

(future)	2014							
Petrol (Gasoline)								
Euro 1†	July 1992	2.72 (3.16)	-	-	-	0.97 (1.13)	-	-
Euro 2	January 1996	2.2	-	-	-	0.5	-	-
Euro 3	January 2000	2.3	0.20	-	0.15	-	-	-
Euro 4	January 2005	1.0	0.10	-	0.08	-	-	-
Euro 5	September 2009	1.000	0.100	0.068	0.060	-	0.005**	-
Euro 6 (future)	September 2014	1.000	0.100	0.068	0.060	-	0.005**	-

* Before Euro 5, passenger vehicles > 2500 kg were type approved as light commercial vehicles N_1-I

** Applies only to vehicles with direct injection engines

*** A number standard is to be defined as soon as possible and at the latest upon entry into force of Euro 6

† Values in brackets are conformity of production (COP) limits

Emission standards for light commercial vehicles

Tab.7 EES for light commercial vehicles ≤1305 kg (Category N1-I), g/km

Tier	Date	CO	THC	NMHC	NOx	HC+NOx	PM	P
Diesel								
Euro 1	October 1994	2.72	-	-	-	0.97	0.14	-
Euro 2	January 1998	1.0	-	-	-	0.7	0.08	-
Euro 3	January 2000	0.64	-	-	0.50	0.56	0.05	-
Euro 4	January 2005	0.50	-	-	0.25	0.30	0.025	-
Euro 5	September 2009	0.500	-	-	0.180	0.230	0.005	-
Euro 6 (future)	September 2014	0.500	-	-	0.080	0.170	0.005	-
Petrol (Gasoline)								
Euro 1	October 1994	2.72	-	-	-	0.97	-	-
Euro 2	January 1998	2.2	-	-	-	0.5	-	-
Euro 3	January 2000	2.3	0.20	-	0.15	-	-	-
Euro 4	January 2005	1.0	0.10	-	0.08	-	-	-
Euro 5	September 2009	1.000	0.100	0.068	0.060	-	0.005*	-
Euro 6 (future)	September 2014	1.000	0.100	0.068	0.060	-	0.005*	-

* Applies only to vehicles with direct injection engines

2.6.3 Fuel Effects on Emissions

Internal combustion engines (ICE) mainly consume fossil fuels, generally gasoline and diesel fuel.

Modem automotive fuelsmust satisfy various requirements, such as: to enable fast refueling; effectively mix with the air; fluently pass from the tank to the engine cylinders; efficiently burn in the cylinders to produce adequate power and minimal amounts of pollutants in a wide range of ambient conditions. The main features required from automotive fuels, following from these demands, are summarized in Tab. 8 (Sher 1998, Guibet 1997).

Tab. 8 Main features required from automotive fuels

Feature	Relationship with engine and vehicle performance
Good combustionquality	Better ignition and combustion qualities lead to better vehicle fuel economy and less emission of pollutants. High octane or cetane numbers are critically important for good combustion quality in SI or CI engines.
Minimized depositformation	Assists in maintaining engines close to their designed optimal efficiency and relieves the deterioration of performance, fuel economy, and emissions. Deposit control additives are low-cost, widely recognized means for suppressing deposit formation.
High heat ofcombustion	A smaller fuel quantity needs to be carried in the vehicle tank when its chemical energy content is high.
Suitable latent heat of vaporization	High latent heat of vaporization causes the charge to be cooled and therefore to become denser. However, there is danger of freezing ambient moisture in the carburetor.
Good performance at high and low temperatures	A fractional composition of fuel must enable easy cold start, good driveability, fuel economy,

	low exhaust and evaporative emissions, and reliable hot restarting without lubricant dilution in a wide range of ambient conditions. Usually, fuels are blended appropriately for both seasonal and geographical variations in temperature.
Materialscompatibility	Materials compatibility is essential for preventing corrosion of fuel system components.
Stability	Better fuel stability enables minimizing deposit formation and storing fuel without deterioration for longer periods of time.
Low foamingtendency	Low foaming tendency is relevant for diesel fuels, enabling faster vehicle refueling with lower evaporative emissions.

Tab. 9 Summarizes the main gasoline and diesel fuel properties that have essential effects on engine exhaust emissions

Gasoline	**Diesel fuel**
Lead content	Sulphur content
Sulphur content	Density
Oxygenates content	Aromatics content
Aromatics content	Cetane number
Benzene content	Distillation characteristics
Olefins content	
RVP	
Distillation characteristics	

2.6.4 Main Fuel Properties Affecting Engine Exhaust Emissions

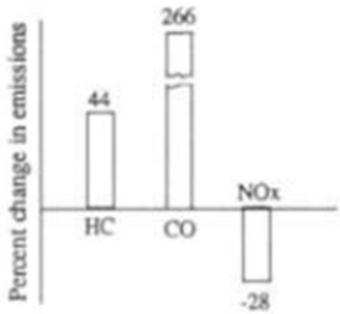
The evolution of modern transportation technologies would be impossible without the development of lubricant additives. Lubricant additives are essential ingredients in modern lubricants - performance products that help maintain engines, transmissions and after treatment equipment in design condition for as long as possible. This improvement of system durability

permits more effective use of energy resources, provides low levels of exhaust emissions, and provides opportunity to use alternative fuels. (ATC Document 49, 2007).
Additives to petroleum have a great role in treatment of fuels intended at improving their properties in order to meet required specifications and to give them additional competitive benefits. The use of additives reduces engine exhaust emissions in many cases.

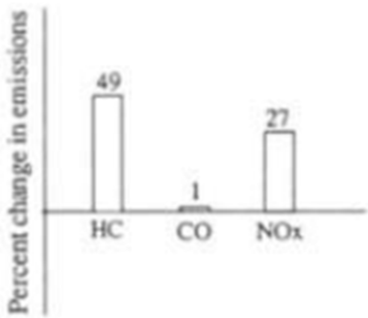
Gasoline additives according to their functional applications can be classifiedto some main groups (Gutman 1992):

- additives protecting fuel systems;
- additives influencing combustion;
- additives improving oxidation stability;
- additives improving lubrication;
- additives used in gasoline distribution.

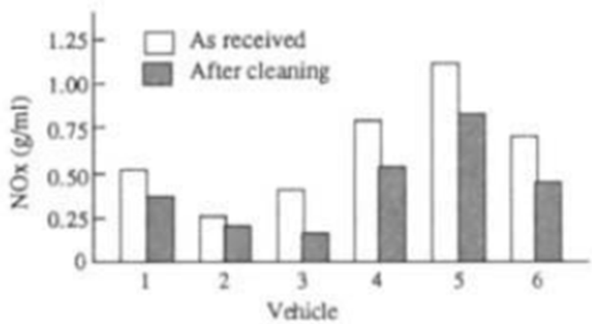
This classification is quite approximate, and exist other classification approaches. For example, deposits control additives (for cleaning both the combustion chamber and the fuel system) may be selected as a separate and important group of additives or to the group of additives influencing combustion we can includeantiknock additives, anti-ORI additives, antipreignition, antimisfire, and spark-aid additives together with additives that improve fuel distribution between cylinders. Most of the additives of all groups have generally a positive influence on emissions.
The group of additives intended to protect automobile fuel systems generally includes deposit-control additives, corrosion inhibitors, and anti-icing additives. Due to ecological matter the use of deposit-control additives became more popular. Deposit formation in carburetors or fuel injectors (especially port fuel injectors), intake manifolds, ports, and on the valves adversely affect engine performance and, in particular, pollutants emission (Fig. 23). The use of deposit-control additives to gasoline allows engine systems to be kept clean and, therefore, in-service vehicle emissions to be brought as close as possible to the designed levels. In order to ensure fuel system cleanliness, detergents to petrol are usually used. These additives are based, as a rule, on polyetheramine, succinimide, or polybuteneamine technologies (Sher 1998, Owen 1995).



1. Injector deposits (injector restriction 23%) (Sher 1998);



2. Intake valve deposits- IVD (IVD rating change from 9-10 to 6) (Peyle 1991);



3. Intake manifold deposits, reproduced from (Peyle 1991).

Fig. 23 Influence of deposits on engine exhaust emissions

2.6.5 Lubricant consumption control

Among significant contributions to fuel economy, conservation of petroleum resources, with concomitantreduced contribution to emissions, is achieved by enhancing lubricant economy in service (Tab. 10). Modern engine designs influence on challenges in lubrication for additive chemistry to control deposits and wear, and maintain long-term low emissions performance. The combination of reduced oil consumption and extended drain intervals greatly increases the load on the lubricant (Fig. 24) (ATC Document 49, 2007).

Tab. 10 Engine oil use trends

Engineering and Lubricant Additive Development Higher performance, with reduced lubricantquantity for gasoline passenger cars (data based on top specification engines)				
Model year	1949	1972	1992	2005
Power (kW)	25	74	96	120
Power density (kW/L)	21	37	45	60
Oil fill (L)	3.0	3.7	3.5	3.5
Oil consumption (L/1,000km)	0.5	0.25	0.1	0.1
Oil change interval (km)	1,500	5,000	15,000	30,000
Oil flush at oil change	Yes	No	No	No
Total oil used after 30,000km (L)	87.0	29.8	10.0	6.5
Average fuel consumption (L/100km)	12	10	7	7
Engine durability (1000km)	<100	175	250	250

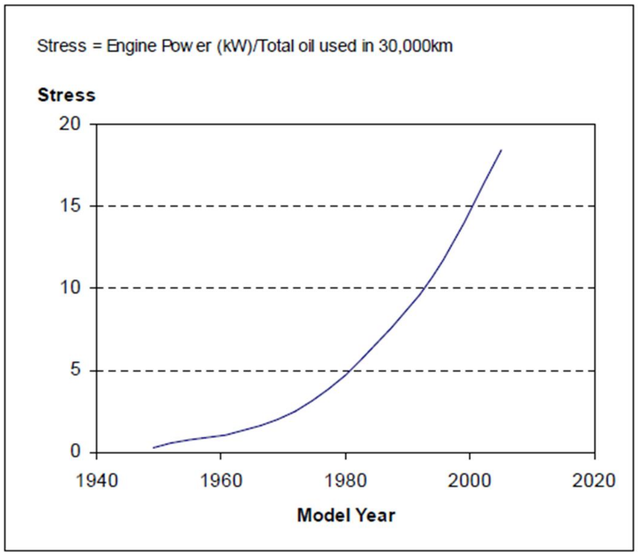


Fig. 24 Stress on passenger car lubricant

Reduction of oil consumptionis achieved by using of lubricant additives. It occurs because of modifying the physical properties of the lubricant such as viscosity. Maintaining systems integrity is a key function of the lubricant. Losses due to leakage have been almost eliminated with the help of oil-seal compatible lubricants. Additive components also assist incontroling wear and deposits, maintaining low oil consumption throughout a vehicle’s life (ATC Document 49, 2007).

2.6.6 Lubricant additives - user benefits

“Lubricant additive technology delivers significantbenefits to the consumer in controlling costsassociated with vehicle design and operation. Thecost of lubricant represents a small fraction of thetotal operating cost of the vehicle. Lubricantadditives reduce consumer costs by reducing fueland oil consumption, lowering maintenancerequirements, extending service intervals, reducingdowntime losses and enhancing vehicle reliability. Lubricant additives provide substantial benefits tothe environment and to the end use”(quoted form ATC Document 49, 2007).

In general additives:

- Improved fuel economy
- Reduce maintenance;
- Reduce pollution.

3. AIM

The aim of this diploma work is to examine and evaluate the two main engine cleaning methods, which are cleaning-in-place method (with use of detergents and additives) and demountable method. To obtain better understanding of engine performance and engine problems (mainly cylinder piston group deposit and engine exhaust emissions).

Main fuel properties affecting engine exhaust emissions, additives for diesel and petrol fuels and their influence on environment are taken into account in this work.

4. MATERIALS AND METHODS

Data and materials provided for experiments were taken from Moscow State Agroengineering University laboratories, Moscow and also from my own previous research and analyses. Automobile taken to show cleaning-in-place method is Hyundai Elantra 2005. Equipment for measuring compression was simple compression tester; set for cleaning included Decoking LAVR ML-202 Anti Coks and Engine Wash Motor Flush

Technology of cleaning in-place method on the example of a petrol engine:

Automobile for decoking: Hyundai Elantra.
Engine: 1.8 liter., Injector, 4-cylinder, cylinder arrangement - vertical.
Drive: Front;
Operational kilometers: 152000;
Year of manufacture: 2005;

Units and assemblage involved in the process:

- Spark plug holes and the ignition wires (highlighted in red);
- Ignition distributor (highlighted in blue);
- Air filter (highlighted in white);
- Timing belt of gas distribution mechanism (highlighted in green);
- Oil filler (highlighted in yellow).

Plan of experiment:

1. Diagnosis of the CPG initial parameters:
   a) spark plugs checkup;
   b) compression metering;
   c) piston surface visual inspection.
2. Engine decoking process:
   a) spark plugs unscrewing and piston installation in midposition;
   b) ignition system disabling;
   c) metering and filling of carbon removing liquid;
   d) start-up of an engine;
   e) oil change.
3. Diagnosis of the CPG initial parameters after decoking.

Experiment:

1. Start with initial parameters diagnosis:

a) Remove spark plug wires connector and unscrew spark plugs;

We carry out an inspection of plugs. In all cases- "standard" light deposition on the points and thin layer of dry sludge on the surface of the base.

b) For compression metering switch out ignition system by removing the terminals from the ignition coils. In this case, access to the terminals is limited by air filter housing, which should be removed.

Latch gears are different for different manufacturers. In our case, the lock latch can be opened by hands. In other cases, you may need a screwdriver. Mechanisms are reliable and designed for multiple opening/closing.

After the ignition system is turned off, we are making compression metering for all four cylinders. Accomplish this twisting compression meter instead of plug and motoring in idle speed with ignition key. Usually you need at least 5-6 engine revolutions.

Compression meter (compression tester) - is an instrument for measuring the maximum pressure generated by the piston during compression. Its indications – is the most important characteristic in assessing of the cylinder-piston group (CPG) condition. Recording the results (12.1, 13.0, 13.2, 11.0).

c) Now carry out visual inspection of the piston surface through the spark plug hole. In our case, spark plug port passes through the oil cover, that is why the distance to the piston is big enough and we have to use light emitted diode (LED). Frequently, the spark plug port is absent and to evaluate the piston surface is not too difficult. Sometimes, in case of angular position of cylinders you can see conditions of its sidewalls. Thus, we see significant amount of dry carbon deposits.

2. Now proceed to engine decoking process. We are going to use the Set: Decoking LAVR ML-202 Anti Coks + Engine Wash Motor Flush:

In this set we have:

- Engine cleansing agents;
- Lubrication system cleansing agents;
- Filling gun, tubule;
- Application instruction;
- Hood sticker for decoking data registration;

a) Before pouring the fluid it is necessary to post pistons horizontally and the in the midposition. In our case to put the car on a flat surface is enough.
b) The ignition system was disabled during compression measuring, pistons position was aligned, so we can start with decoking argent dispensing into the cylinders.
c) Fluid dispensing fulfills with the filling gun and tubule. The volume of argent is 45ml. for each cylinder.

Lightly twisting spark plugs after adding the washing fluid. Thus, we close the output of the active components due to evaporation and create a very "thin" and the important effect of " vapor area" - impact on the carbon deposits which are located above the filled fluid: valve surface, cylinders side walls, spark plugs, injection nozzle, etc.

The effectiveness of the fluid is proportional to the exposure time and engine temperature. The minimum possible exposure time is 1 hour. Usually it is easier to carry out decoking for 12 hours (" during the night"). The longer time of engine cooldown the better. Also for better decoking effect it is recommended to move pistons up and down for 2-3 hours, turning crankshaft in both directions in the range of 5-10 degrees. Decoking was last for 2 hours.

After this time, we have to unscrew the spark plugs. Carry out the visual inspection of plugs. As you can see, the deposition on the contacts disappeared, and spark plug base soot impregnated with the composition and it is in the loose and turgid state. This sludge can be easily removed by fingers.

We still have to remove excess fluid and vapor from the cylinder. For this we cover spark plugs holes (candles are unscrewed) with a duster, and scroll engine shaft with starter 2-3 times for 5-10 seconds. Fluid from the cylinder releases into the duster without adjacent units and parts contamination.

Now it is possible to inspect the piston surface. As you can see, sludge is soft and in turgid state, well-saturated with the composition.

d) In the end we have to assemble all units and parts in original construction and crank engine for 5 minutes. At this stage it is not recommended to increase the engine speed above 2/3 of the maximum. Here, we did not have any problems.

e) All that is left to do is to change oil in the system. For changing oil we use a special concentrate for oil system cleaning.

Steps:

- Warming up engine up to working temperature;
- Filling the concentrate into oil-filler (an average one pack for 3.5-4 liters of oil);
- Starting engine and give running for 5 minutes;
- Returning old waste oil and filling with the new one

3. Finally we check the level of compression. As you can see, now everything is in normal conditions: 14.0, 14.0, 14.5, 14.0.

Demountablemethod of engine cleaning:

This cleaning method is long-term process, which includes more heavy works.

Operation stages are presented in the following Tab. 11.

Tab. 11 Standard Specifications for CPG cleaning

№	Name of operation	Steps of maintenance operation	Tools	Standard Specifications
1.	Mechanical work	Unscrew spark plugs	Cloth, tension indicator with detachable heads	Accurately, without effort unscrew spark plugs, carefully to make sure that tension indicator grips plug's hexagon drive
2.	Diagnosis	Check compression	Compression meter, cloth	Compression ≥ 0.6 MPa
3.	Mechanical work	Remove cylinder head, remove pistons	Cloth, tension indicator with detachable heads	-

4.	Cleansing	Soften contamination with liquid petroleum oil and then remove it with polishing paper	Liquid petroleum oil, polishing paper	Surface should be cleaned of carbon deposit
5.	Diagnosis	Visible inspection of components	-	-
6.	Assembly work	Set down pistons and cylinder head	Cloth, tension indicator with detachable heads	Piston with piston rings drive in with force about 5N-7N
7.	Checking operation	Check compression	Compression meter	Compression ≥ 1.0 MPa
8.	Mechanical work	Unscrew spark plugs	Cloth, tension indicator with detachable heads	Install as far as it will go, without effort and fasten down

5. RESULTS AND DISCUSSIONS

To obtain a better understanding of both methods, I will also provide some results taken from previous researches.

Theoretical explanation of oil additives effectiveness (example was taken from 360ip company researches).

Problem:

Because of increasing in the number and variety of vehicles, the problems with fuel consumption and environmental pollution have became more noticeable. The use of an energy-conserving and emission-reducing automotive engine oil additive would have a great impact on energy conservation and environment protection. Nonetheless, such an additive would need to strengthen the most important lubrication properties, such as low-temperature performance, viscosity index, high temperature performance and oxidation resistance.
The tests were conducted in accordance with QC/T 524-2005, Testing Methods for Automobile Engine Characteristics. The nanoparticle additive was added to 10W-40 engine oil and its performance was compared with the same 10W-40 engine oil but without additive.

Tab. 12 Gasoline engine characteristics with and without oil additive

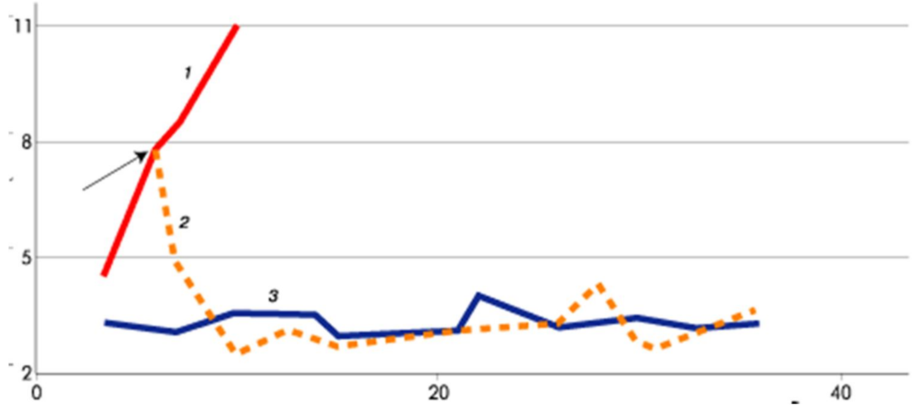
N_0	RPM	Engine Oil	Torque/ N.m	Power/ kW	Fuel Consumption g.kwh	Fuel consumption reduction	Torque increase	Power increase
1	4500	10W-40	133.92	63.11	302.17	5.3%	3.5%	3.4%
		10W-40 +Additive	138.57	65.27	286.06			
2	4000	10W-40	129.57	54.27	314.89	9.0%	6.5%	6.5%
		10W-40 +Additive	137.93	57.8	286.55			
3	3500	10W-40	139.77	51.23	257.15	7.1%	3.8%	4.7%
		10W-40 +Additive	145.1	53.63	238.85			
4	3300	10W-40	139.8	48.31	247.15	5.2%	4.1%	4.0%
		10W-40 +Additive	145.56	50.26	234.25			
5	3000	10W-40	140.38	44.1	242.96	5.9%	4.4%	4.4%
		10W-40 +Additive	146.57	46.02	228.73			
6	2700	10W-40	143.08	40.47	236.71	5.1%	3.4%	3.5%
		10W-40 +Additive	147.97	41.89	224.73			
7	2500	10W-40	143.64	37.61	235.02	5.1%	3.5%	3.5%
		10W-40 +Additive	148.65	38.93	222.92			
8	2300	10W-40	140.37	33.8	235.64	5.4%	3.5%	3.8%
		10W-40 +Additive	145.3	35.1	222.85			
9	2000	10W-40	134.51	28.17	239.08	5.3%	3.6%	3.7%
		10W-40 +Additive	139.3	29.22	226.36			
10	1800	10W-40	134.55	25.37	237.11	5.0%	3.5%	3.4%
		10W-40 +Additive	139.26	26.24	225.23			
11	1500	10W-40	128.5	22.17	247.62	9.5%	6.8%	6.9%
		10W-40 +Additive	137.3	23.7	224.1			

From the Tab. 12 we can notice following results:

- Increased engine power by 3.4%-6.8%;
- Increased torque by 3.4%-6.9%;
- Reduced fuel consumption by 5%-9.5%;

Also the effectiveness of additives we can see through the following figure, which present results of carbon monoxide concentration in the exhaust gases of injector engine gasoline (petrol) powered with additives and without. Moreover it shows how is this indicator is influenced by the adding detergent while in engine operation.

Concentration CO_2, %



Time, h

Fig. 25 The concentration of carbon monoxide in the exhaust gases under the test bench:

1- Petrol engine without additive;

2- Petrol engine with additive (moment marked with an arrow)

3- Petrol engine with detergent.

Additives Influencing Diesel Fuel Combustion

“Cetane (ignition) improvers are used to improve the cetane quality of marketed fuel components by reducing the delay between injection and ignition when fuel is sprayed into the combustion chamber. These additives are used in two different ways:

1. To increase the cetane number of diesel fuel, which would otherwise fail the specification limits.
2. To increase the cetane number of diesel fuel above the specified minimum standard to yield premium-grade products now being marketed by many oil companies in certain locations throughout the world”(quoted from Sher 1998).

Nitrates (especifically ethyl-hexyl nitrate (EHN)) are the chemicals that mainly used as ignition improvers. Also certain peroxides have been identified as effective cetane improvers. They are all materials that decompose readily, and at elevated temperatures they generate free radicals that accelerate oxidation of the fuel and initiate combustion. The response to cetane improvers is dependent on cetane level and on the individual fuel characteristics. “Results presented in Fig. 26 were obtained from a large sample of fuels and show that, on the average, an improvement of about three numbers was obtained with a treat level of500 ppm, and with 1000ppm the gain was five numbers” (quoted from Sher, 1998). The results show that fuels with lower-cetane index have poorest response and also we can see considerable variation about the average line.

Moreover, we can see from the figure, is that the same cetane number produces the same ignition delay notwithstanding of whether the former is that of the base fuel or a treated one.

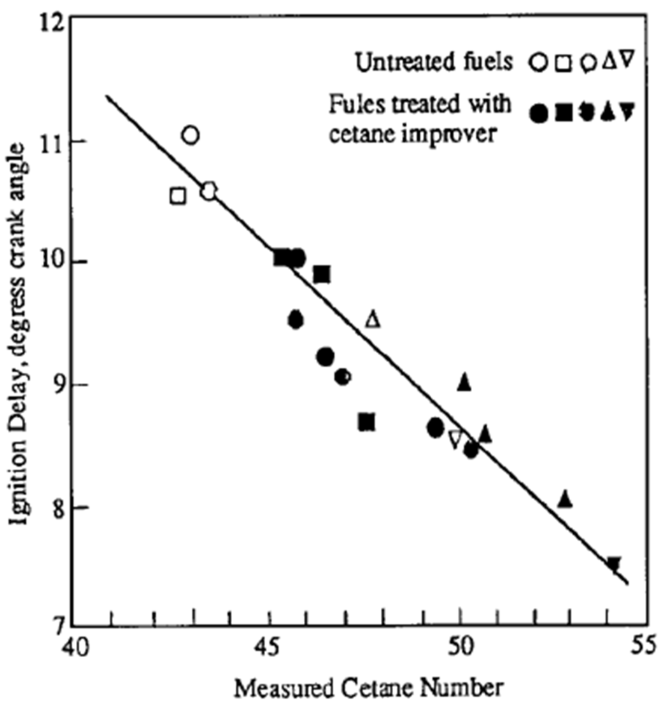


Fig. 26 Influence of cetane number on ignition delay (Sher 1998)

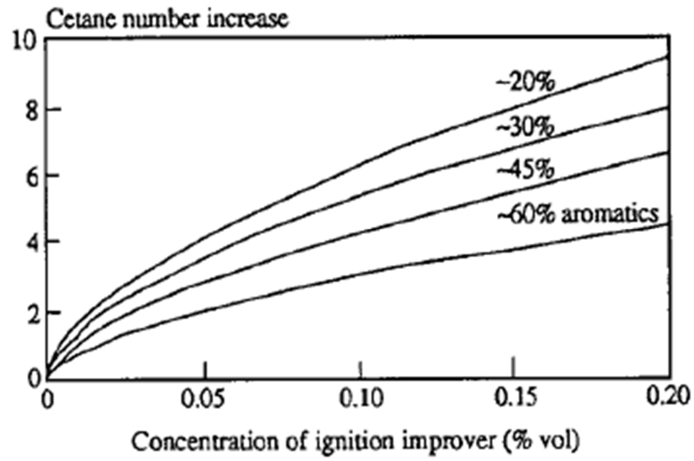


Fig. 27 Response of different base fuels to ignition improvers (Gairing 1995)

On the Fig. 27 first of all, we can see monotonic relation between the concentration of the ignition improver ERN and the cetane number for various chemical compositions of the fuel and secondly, increasing of ERN amount reduce improvements in comparison with initial amount. In practice, for example, the cetane quality of typical European market diesel fuels can be increased by about two to four units using 500 ppm of ERN as shown in Fig. 28 (Gairing 1995).

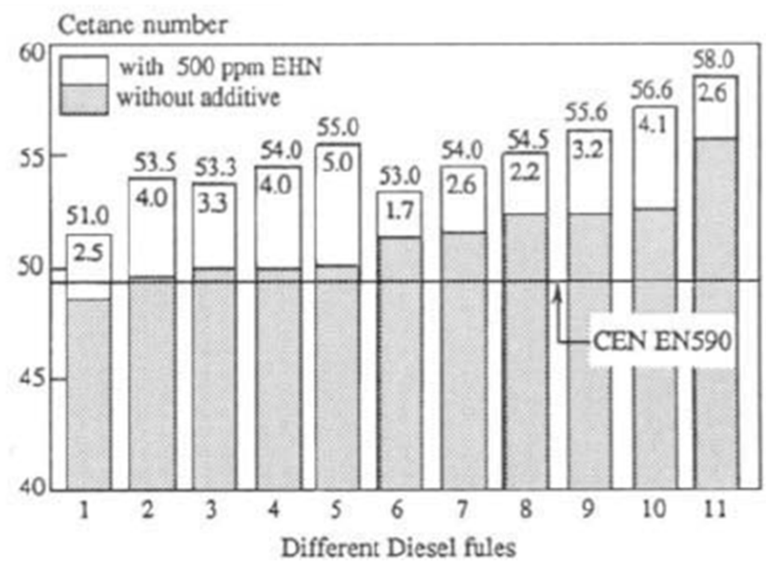


Fig. 28 Increasingcetane number by adding ignition improver for different European diesel fuels (Gairing 1995)

Detergent Additives (detergents)

Detergency is an important property of the reformulated diesel fuel (called also premium or low emission). The use of detergent additives has become widespread in Europe during the last decade. It was caused by problems of coking. Nozzle coking is induced by thermal degradation of fuel and crankcase lubricant components, and worsened by hot combustion gases. This results in slower initial combustion and pressure rise delay in the cylinder, with subsequent increased rate and higher peak pressure (Sher 1998, Vincent 1994). These effects are resulted in increased emission of pollutants, engine noise, and fuel consumption. “Detergent/dispersant additives containing surfactants can prevent deposit formation ("keep-clean"), and remove detrimental deposits already formed ("clean-up") in fuel injectors. Thus, they yield and ensure good spray pattern characteristics, and maintain engine performance and pollutants emission at the best levels possible for in-use engines. A range of substances is now suitable as detergent additives for diesel fuels: amines, imidazolines, amides, fatty acid succinimides, polyalkylenesuccinimides, polyalkyl amines, polyether amines, and so on” (quoted from Sher 1998). Testing and evaluating such additives is the main aim for improvement product quality. “Care must be taken when selecting additives in order to avoid any problems created by adverse side effects resulting from their addition to the base fuel” quoted from Herbstman 1991). There are two test methods which are mainly applied for performance evaluation of detergent additives. In Europe, the test is based on the widely used Peugeot XUD 9 1.91 light-duty IDI diesel engine, and in the United States on the Cummins L-10 engine (Vincent 1994).

The detergent influence on emission performance is illustrated by a test vehicle, which was operated under part-load, city-type driving conditions with and without a detergent in the fuel (Fig. 29). We can see that fuel with detergent additive shows relatively constant emission level however, the base fuel shows augmentation in particulates emissions over the test periods (Sher 1998).

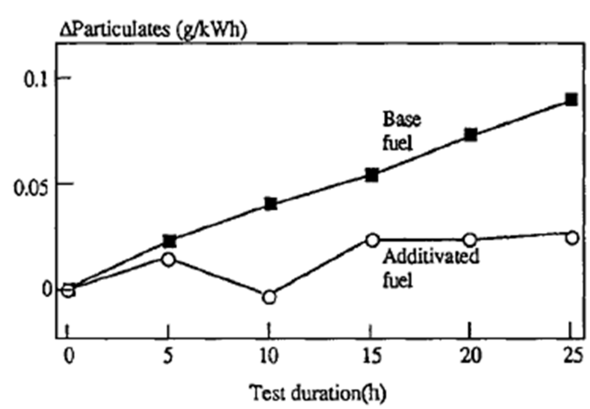


Fig. 29 Effect of diesel fuel detergent additive on particulates emissions (Gairing 1995)

6. CONCLUSIONS AND RECOMMENDATIONS

Conclusions

Based on the results in this diploma work and my previous researches, it was analyzed and concluded that cleaning –in-place engine cleaning method has more advantages in comparison with demountable method.

The last one is very laborious and requires a lot of time and highly qualified staff. In order to reduce labor costs, increase productivity, reduce complexity in maintenance inspections and car operating repairs, was used cleaning-in-place engine cleaning method. It based on usage of various additives and detergents that may affect in following ways:

- intensify the positive characteristics of oil and give necessary new properties (oil additives);
- influence on carbonmonoxide concentration (detergents) ;
- improving low-temperature properties of diesel fuels;
- prevent the formation of carbon deposits in the combustion chamber;
- prolong the endurance of fuel system (anti-wear additives);
- influence on cetane number (cetane-improvers).

Moreover, in this paper was presented chemical composition of lubricant additives and performed analysis of influence of harmful agents formed during the fuel combustion on the environment and the human body, including the comparison of fuel characteristicswith using of additives/detergents and without their use.

Recommendations

1. There are some steps you can do to produce lowest possible emissions:
    - Check tires pressure regularly. Keep your tires inflated to their recommended pressure;
    - Avoid idling because it wastes fuel and produces additional pollution.
    - Shut off the engine during traffic delays or while conducting drive-up transactions;
    - Use detergents and fuel additives;
    - Drive sensibly and observe speed limits, because driving fast can significantly reduce your fuel economy.
    - Perform regular vehicle maintenance;
    - Minimize vehicle weight and maximize aerodynamics because adding mass to a car also decreases fuel economy.

2. Do not use additives and detergents if wear rate of parts and machinery units is more than 80%;

3. Use of high-quality gasoline, because low-qualitygasoline with added additives may causesignificant problems for automobile.

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IV.**APPENDIX**

Tab. 1 Review of detergents and fuel additives used in Europe

FOR PETROL ENGINES  **SPEED TEC PETROL**	**FOR CARBURETOR ENGINES**  **CARBURETOR AND VALVE CLEANER**	**FOR FUEL INJECTION ENGINES**  **INJECTION CLEANER**	**FOR PETROL ENGINES**  **FUEL SYSTEM TREATMENT**
Modern petrol additive for improved, smoother acceleration and throttle response in the partial-load range. Increased driving enjoyment due to higherperformance. Simply add to petrol. Sufficient for up to 70 liters of petrol. ***Effects:*** *Faster combustion;* *Higher performance;* *Reduces non-combusted residual fuel.*	Removes deposits in the combustion chamber, carburetor, on intake valves and on spark plugs. Keeps the engine clean. Regular use assures low smog test exhaust emissions. With long-time effect: add to petrol every 2000 km when filling up. ***Effects:*** *Higher engine performance.* *Lower petrol consumption.* *Corrosion protection.* *Lower pollutant*	Removes carbon and other deposits from fuel distributor/throttle body, and from injectorsand valves. Providesfor precise injection meteringand fuel spray pattern. Regularuse guarantees lowest smogtest emission levels. With longtimeeffect: add to petrol every2000 km – when filling up. ***Effects:*** *No more starting problems and no more lean surging and hesitation.* *Smooth idling, good throttle response.*	For preventive care, add to the fuel every 2000 km. Sufficient for max. 75 liters of fuel. Highlyeffective combination ofadditives protects all components of the fuel system against corrosion. Catalyst convertertested. ***Effects:*** *Assures optimum drivability and low fuel consumption.* *Guarantees low levels of pollutants in the exhaust gas.*

	emissions.	*More engine power. Fuel consumption is reduced. Environment-friendly combustion.*	*Maintains engineperformance. Assures optimum mixture preparation. Enhances operating reliability and economy.*
FOR PETROL ENGINES 	**FOR PETROL ENGINES** 	**FOR PETROL ENGINES** 	**FOR PETROL ENGINES** 
VALVE CLEAN Prevents deposits at valves and keeps the engine clean. Provides ideal fuel utilization band clean burning. Regular usage gives low smog test exhaust levels. Use at every filling. Sufficient for one tankfull.	OCTANE PLUS For all petrol-driven motors for the improvement of the performance. Reduces knocking combustion from petrols with low octane numbers. First add OCTANE PLUS and then top up, which provides optimal independent mixing. 150 ml sufficient for 50 l petrol.	FUEL PROTECT Protects petrol fuel system against water and waterbornecontamination. Protects against rust, corrosion and wear. Preventsicing in fuel lines, filtersand carburetors.	LEAD SUBSTITUTE For all petrol engines that previously needed leaded petrol. To be added when filling up. Avoid undertreating and overtreating. 25 ml is sufficient for 25 l of petrol.

***Effects**:* *Lower petrol consumption.* *Lower pollutant emissions.* *Corrosion protection.* *No pinging, knocking or hesitation.*	***Effects**:* *Increases the RON by up to 4 points.* *No harmful effects on catalytic converters.*	***Effects:*** *Keeps fuel system in good working order.* *Works against pluggingof fuel lines and filters.* *Improves cold-start performance*	***Effects:*** *Lubricates and protects unhardened valve seats againstwear and ”recession”. Preventsengine damage. Maintains excellent compression.*

Also company Paramo brought a significant contribution to additives market. Paramosells their products mainly to individual European countries, especially to the Czech Republic, Slovak Republic (72.5 %), Germany (4.85 %) and Hungary (9.2 %). Last year they also launched exports of oils into Russia, Serbia and Sweden. Paramo currently negotiates further deals with other potential foreign oil and plastic lubricants customers, including Ukraine, the Baltic republics, Austria or France. Pardubice refinery is also in touch with business partners in several Asian and African countries.

PARAMO has two plants. Crude oil is processed in Pardubice. Hydrogenated and hydrocracked distillation cuts are processed in Kolín for production of base oils with extremely low sulphur content and lubricants. Our lubrication oils meet the requirements of renowned machinery and equipment manufacturers, such as VW, BMW, GM, FORD, MB, VOLVO, MAN, SCANIA, RENAULT, DAF, CATERPILLAR, TATRA, TEDOM, DAEWOO AVIA, ZETOR, and others.

The following table shows some products of this company:

Tab. 2 Diesel Engine Oils

MOGUL	SAE	Product Specification
RACING 5W-30	5W-30	Extreme-high performance synthetic motor oil for extended oil change intervals (Longlife III) and for automobiles with DPF. This oil meets special requirements for higher fuel economy as well as ecological requirements for road traffic
RACING 5W-30 F	5W-30	Extreme performance, low-viscosity synthetic motor oil. Special formula for FORD cars. It is suitable for engines with catalytic converters.
FELICIA	15W-40	Universal all-year-round oil for modern petrol and diesel engines; its formula has been developed to suit Škoda cars. This product delivers an exceptionally good price utility ratio.
SPECIAL 20W-30	20W-30	Oil for lubrication of older types of petrol or diesel engines with moderate to lower requirements for oil performance.
DIESEL L-SAPS 5W-30	5W-30	Synthetic, low-viscosity oil for lubrication of dieselengines operating under extreme load that require Low-SAPS oils (low content of sulphated ash,

		phosphorus, and sulphur). It is suitable for engines fitted with SCR systems and for EGR engines with or without DPF This product allows meeting the strict emission limits of EURO IV and V; it also guarantees very long oil servicing intervals.