

DEPOSIT FORMING TENDENCY IN SPARK IGNITION ENGINES AND EVALUATION OF GASOLINE DETERGENT ADDITIVES EFFECTIVENESS

Zbigniew Sępień

*Oil and Gas Institute, Performance Testing Department
Engine and Tribology Tests Laboratory
Lubicz 25 A, 31-503 Krakow
phone: +48 12 6177463, fax: +48 12 6177522
e-mail: stepien@inig.pl*

Stanisław Oleksiak

*Oil and Gas Institute, Performance Testing Department
Lubicz 25 A, 31-503 Krakow
phone: +48 12 6177429, fax: +48 12 6177522
e-mail: oleksiak@inig.pl*

Abstract

The paper describes influence of legislation requirements on development of spark ignition engines construction and new expectations towards today's fuels and detergent-dispersant additives. Paper presents development history of fuel additives especially of detergent additives. It indicates most critical places of engine deposits formation and its impact on fuel consumption, emission and vehicle driveability. It describes also the most popular engine tests methods for evaluation of deposits forming tendency on intake valves and combustion chambers and detergent additives effectiveness, focusing on CEC (Coordinating European Council for the Development of Performance Tests for Transportation Fuels, Lubricants and Other Fluids) test methods by using of Mercedes M102 (CEC F-05 - 93 - Inlet Valve Cleanliness in the MB M102E Engine) and M111 engines (CEC F-20 - Test Method For Inlet Valve Cleanliness). CEC test methods has been approved both by fuel producers and engine and vehicles manufacturer, what is noted e.g. in World Wide Fuel Charter. From many years in major of these Groups, representatives of Oil and Gas Institute (earlier as Petroleum Processing Institute) had an active part.

Deposits formed in the injectors, intake valves and combustion chambers of gasoline engines can cause various performance and emissions problems.

Keywords: *combustion engines, deposits, detergent additives, engine fuels, test methods*

1. Introduction

The topic of discussions which have been continued from many years is carbon dioxide emitted by automotive engines, its influence for greenhouse effect and followed from this settlements recorded into Kyoto Protocol. These settlements oblige of car manufactures to taking steps tending to reduction of vehicle fuel consumption. At the same time are progressively put into execution repeatedly severe regulations concerning emissions standards for vehicles both in Europe (Tab. 1), and in USA (ULEV and SULEV). So, European and national legislative bodies are forcing the industry to pay serious attention to potential sources contributing to emissions from road transport. To meet the increasing demand, car producers are constraints for incessant improvement of engine construction and initiating a new engineering which in turn forcing shifts in fuels production technology.

It is well known, that any material creating from products of the fuel and/or engine lubricant,

accumulates in the carburettor or fuel injectors of injection system, intake manifold, valve ports, tulip section of the intake valves and in combustion chambers of spark ignition engines.

Tab. 1. EU-Standards for M-Vehicles [1]

Gasoline vehicles ¹⁾	CO [g/km]		HC [g/km]			NO _x [g/km]	
EU 3	2.3		0.2			0.15	
EU 4	1.0		0.1			0.06	
	CO [mg/km]	THC+ NO _x [mg/km]	THC [mg/km]	NMHC [mg/km]	NO _x [mg/km]	PM ^{2,3)} [mg/km]	PN ⁴⁾ [x/km]
EU 5	1000	–	100	68	60	5.0/4.5	–
EU 6	1000	–	100	68	60	5.0/4.5	⁵⁾

¹⁾ Valid also for CNG & LPG vehicles.

²⁾ PM standard for positive ignition engines applies only to vehicles with direct injection engines.

³⁾ A revised measurement procedure shall be introduced before the applications of the 4.5 mg/km standard which be apply on 01.09.2011 (new types) and on 01.01.2013 (new registration).

⁴⁾ A new measurement procedure shall be introduced before the application of the PN-standard.

⁵⁾ A number standard is to be defined for this stage for vehicles, with positive ignition before 01.09.2014.

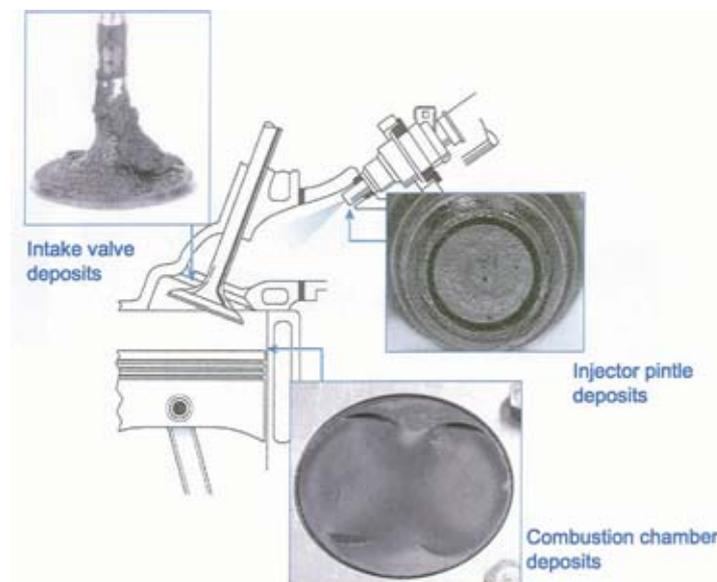


Fig. 1. Location of engine deposits

Most gasoline tend to contribute to deposits in above mentioned engine parts – Fig. 1. Simultaneously, with modern engine technology, lubricant derived deposits are generally negligible. The problem of deposit formation on the elements of combustion chambers, intake valves and induction systems is recognized since at least forty years, taking into account that these phenomena became more important in the 1970's because by introduction of gasoline additives the engine operation could be improved. At that time the most interest induced deposits formed in the intake systems of internal combustion gasoline engines, especially on the intake valves and optionally in the carburettors – Fig. 2.

As emissions standards became more stringent, mechanical and next electronic fuel injection replaced carburetion, what had positive influence for emission lowering and improving of fuel economy and performance. The earliest multipoint port fuel injector designs were prone to deposit formation along the throttling pintles [2]. In the 1980's first field-problems with fuel injected engines were reported caused by intake valve deposits (IVD). A little later has been observed increased tendency to forming of combustion chamber deposits (CCD) which build up in all gasoline engines with use and can affect engine performance and emissions – Fig. 3-6.

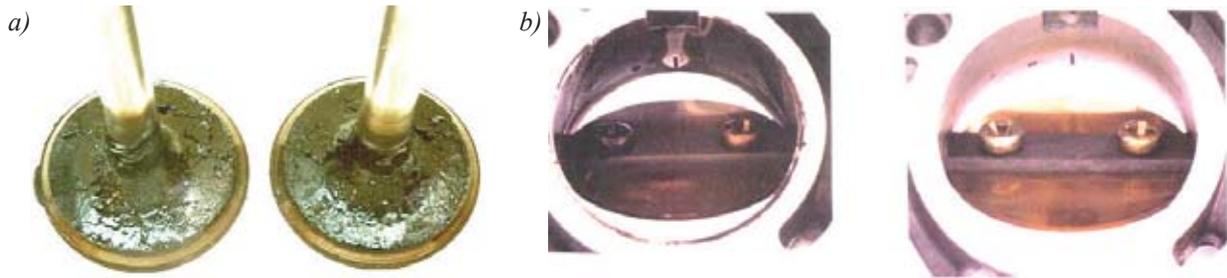


Fig. 2. Intake valve deposits (a), and deposits in the area of carburettor throttle (b) – OPEL Kadett, OHV, 2 – VPC, carburettor [INiG]



Fig. 3. Intake valve deposits – Mercedes-Benz M102E, OHC, 2 – VPC, electromechanical Port Fuel Injection [INiG]

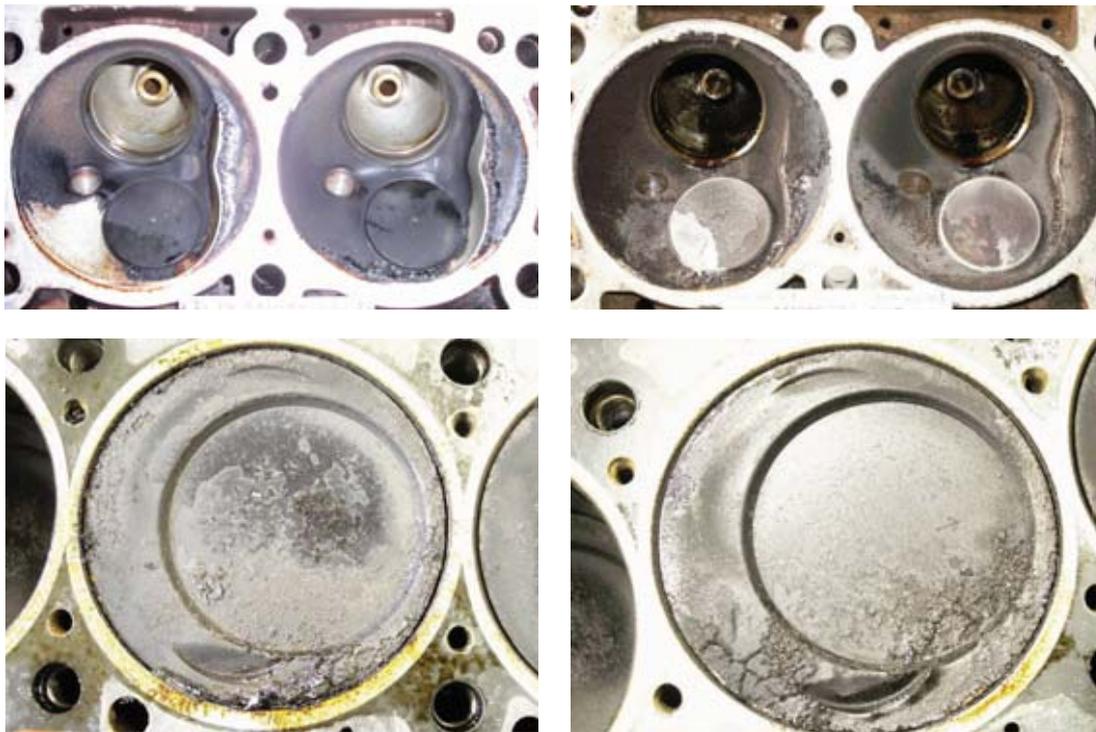


Fig. 4. Combustion chamber deposits and piston top deposits – Mercedes-Benz M102E, OHC, 2 – VPC, electromechanical Port Fuel Injection [INiG]

In spite of the technical issues to gasoline direct injected (GDI) engines engineering as has been reported at the beginning of the 1990's, fuel economy benefits of 15-30%, and resulting lower levels of greenhouse gas CO₂ emissions, as well as power improvement of 10-15% per unit volume of displacement, have provided incentive for continued its development. Then direct injection gasoline engines have become the subject of very intense interest in recent years with commercialization of many models by different manufacturers.



Fig. 5. Intake valve deposits – Mercedes-Benz M111, DOHC, 4 – VPC, electronic Port Fuel Injection [INiG]

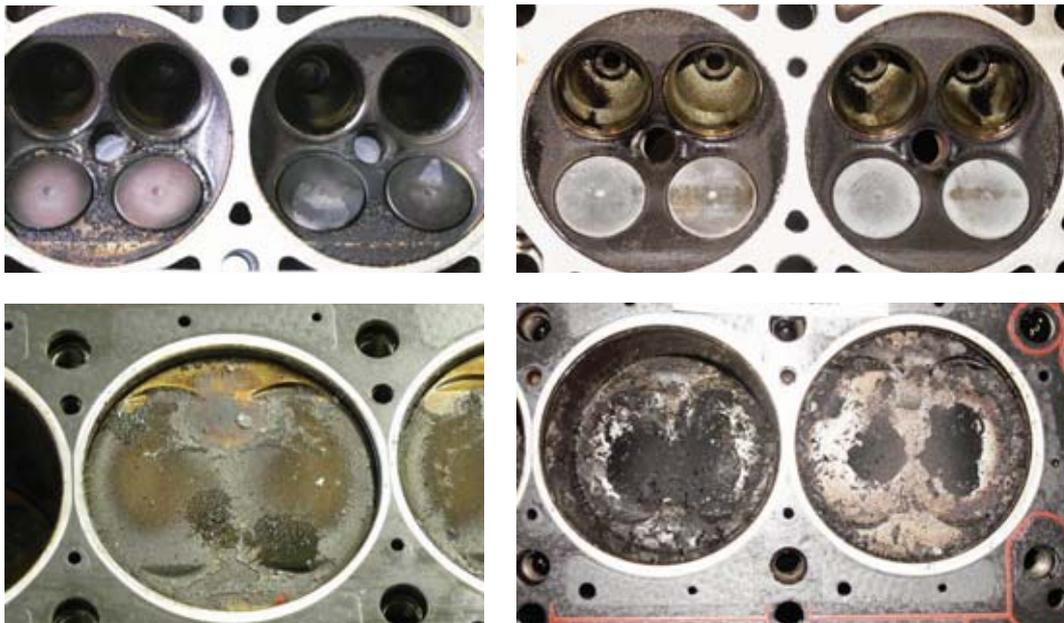


Fig. 6. Combustion chamber deposits and piston top deposits – Mercedes-Benz M111, DOHC, 4 – VPC, electronic Port Fuel Injection [INiG]

Future market penetration of this technology is predicted to increase violently in the future, as these engines offer the promise of higher specific power output, improved fuel economy, lower engine out emissions and improved throttle response compared to conventional port fuel injected gasoline engines [3].

In gasoline direct injection engines, the fuel injectors have been displaced from the intake manifolds or cylinder head ducts into the higher temperature combustion chamber. The higher temperatures and the exposure to the combustion environment increase the risk of forming fuel injector deposits which can affect vehicle performance – Fig. 7 [4].



Fig. 7. Fuel deposits on the tip of GDI injector [4]

In general, GDI engines produce a greater level of deposits in comparison to PFI engines in each of the above mentioned areas, namely fuel injectors deposits, combustion chamber deposits, intake and exhaust valve deposits. With respect to GDI injector fouling, the stratified charge cycle produced a greater level of injector fouling than the stoichiometric cycle. In some publications it is reported that GDI engines produce over twice as much IVD under comparable with PFI lean cycle conditions on base fuel, and about equal amounts under rich cycle conditions [5].

Deposit forming tendency of modern engines is one relevant parameter which causes driveability problems, increases fuel consumption, emissions and noise, reduces the power output and affects the engine durability what causing concern in the automobile industry.

2. Deposits formation and its effects on engine performance and emissions

All engines progressively accumulate engine deposits as a result of the normal gasoline combustion process. CCD and IVD deposit are originated primarily from fuel and to some extent from the engine lubricating oil. Gasoline consists of different hydrocarbons which vary in molecular weight and structure. Under certain environments, some of these hydrocarbons will undergo physical and chemical transformation and form deposits, which in critical areas of the engine can cause performance problems. For fuel derived deposits, the deposit precursors are partially oxidized fuel in the gaseous phase. The primary deposit formation mechanism appears to start with radical initiated addition/substitution reaction on fuel and lubricant components to produce coordinated oxidation products which then condense on the hot surface. Condensation is followed by pyrolysis or polymerization processes. The condensation of deposit precursors on the surface is the critical step in this process and deposit formation is strongly depending on the surface temperature. Higher surface temperature reduces deposit levels. Because of the required condensation process, more deposits will create in the end gas zone, on cold surfaces, with high boiling fuel constituents [6, 7]. Considering mechanism of deposit formation it should be remembered that oil part of deposits forms by losing base oil by evaporation or decomposition, while partially oxidized. Under high temperature conditions, oil additives are condensed and reacted to be inorganic compounds. However under intermediate engine driving conditions, contribution of engine oil, especially of oil additive in deposit formation is for modern engines negligible. Coolant temperature, fuel-air ratio, and first of all boiling point of the fuel have significant influence on both amount and the morphology of deposits formed in a combustion chamber. As the deposits grow, the surface temperature increases because of insulating properties of the deposit. For any given engine conditions, it is the highest boiling fraction of the fuel that contribute most to combustion chamber deposit formation [8]. For given fuel, there will be a maximum surface temperature above which little deposit will form. For example this critical temperature for indolene has been established for 310°C [9] and for other unleaded gasolines for 320°C [10]. Some researchers suggest 325°C as an upper limit for deposit surface temperature during engine operation [11]. For fuels of low boiling point like isooctane or an alkylate this critical temperature is lower than any normally found in the combustion chamber and very little deposit from the fuel will be formed. In contrast, toluene has a high tendency to form deposits. Referring to fuel composition it should be found that aromatic are the most prone, paraffins are the least prone with the olefins between for deposit formation and boiling point is the only factor determining the deposit forming tendencies of aromatics. For lubricating oil, which has a higher boiling point compared to the fuel the critical surface temperature for deposit formation is approximately 60-70°C higher. Engine oils appear to affect the formation of piston top deposits more than the head deposits. It has been shown in our investigations that the commercial deposit control additives can be major source especially CCD, because have higher boiling points compared to the base fuel components and hence will cause an increase in deposit rate. Our observations and research results were consistent with those reported by other researchers [7, 12, 13]. So, for a given engine operating conditions, and hence a surface

temperature regime, if higher boiling point materials, such as some fuel additives are added to a given fuel, more deposits will be formed [6, 10, 14, 15]. It is also likely that additive components deposit directly on to surfaces on which they impinge rather than going through a deposit precursor phase. Deposit growth is a dynamic and reversible process which at a given time, reflects the balance between the formation and removal processes [6]. Different fuels might take significantly different times to reach stabilization in the same engine test and on the various parts of combustion chamber – Fig. 8. For example, the time scale required for stabilization of CCD is quite large for base fuels. The presence of additives reduces this time scale significantly. In a fixed duration test, a large part of the increase in CCD caused by additives could be attributed to this difference in time scales [12]. So, it is important to compare fuels when deposits on the evaluated parts have reached near stabilized levels. Short duration tests could be misleading if the test duration is small compared to the time scale required to approach stabilization. It is also important to consider the influence of base fuel while assessing the effect of additives on deposit formation particularly if incremental effect of additive packages on the base fuel is being considered. In case of fuels including additives, the initial deposit growth rate is faster and the self – correcting mechanism on growth rate also comes in faster so that the deposits reach a stabilized level quicker – Fig. 8.

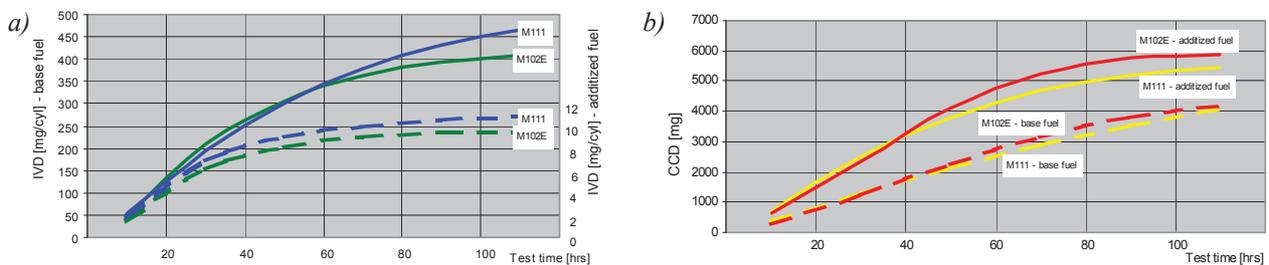


Fig. 8. Comparison of Intake Valve Deposit (a), and Combustion Chamber Deposit (b) for base fuel and additized fuel evaluated in M102E or M111 test engine

Various mechanisms lead to earlier has formed deposits removing. These include chemical mechanisms like oxidation and gasification, physical mechanisms like desorption and evaporation of volatile and gaseous components and mechanical removal like abrasion and flaking – Fig. 9, brought about by thermal stresses and mechanical wash-off [6]. Combustion chamber deposit can flake by interacting with water, which is present in the atmosphere and in the gases in the cylinder from previous combustion, when the engine is not running.

Deposit flaking depends on the temperature regime under which the deposits are formed. So it is possible that fuels which might produce deposits which do not flake in one engine or operating regime might produce deposits which flake in another engine or operating regime with different thermal environment [16]. Combustion chamber deposits flaking causes low compression pressures due to improper sealing of the valves. This problem occurs when pieces of CCD flake off and end up lodged between the valve face and the valve seat. Symptoms of combustion chamber deposit flaking are difficulty in starting and rough running when cold. Some detergent additive packages suppress flaking whereas some additives can promote flaking.

System of direct injection gasoline has itself a significant influence for engine deposit formation, and especially on injector coking. Generally, two main types of GDI design have been stood out that means: “spray-guided”, and “wall and air-guided” combustion systems. Spray-guided systems are characterized by centrally mounted injector located close to the spark plug. The distance of separation is such that the spark ignites the edge of the spray cone. This type of system is more propense to injector coking because of the closer proximity of the injector to the combustion event and to greater amount of fuel remaining on the injector tip. [17]. Wall and air-guided systems have injectors mounted at an angle, and the spray is deflected off the piston top towards the spark plug. This design is less prone to injector coking because the injector achieves



Fig. 9. Examples of deposit flaking in combustion chamber and on the piston top [INiG]

lower tip temperatures because of greater distance to the flame front and greater air movement around the tip reducing the amount of residual fuel [17]. One should be find that in general GDI engine injector fouling is more severe than the manufacturer's comparable PFI engine.

Injector design is a critical factor in terms of susceptibility to the build up of deposits. The trend in modern injector design is to use a greater number of smaller holes to improve atomization and enhance spray patterns, usually to help meet tighter emission standards. Unfortunately, smaller holes tend to be more susceptible to fouling. Deposits formed inside of injector of GDI engines restrict fuel flow and alter spray characteristics of injector. If levels of this flow restriction are too high, any level of spray distortion cannot be adequately compensated by engine control electronic system. As in GDI in contradiction to PFI engines charge flow characteristics in the cylinder are very sensitive to injector spray distortion and are critical to calibrations, for driveability, fuel economy and emissions, fuel injector performance is at the forefront of issues. Fuel composition plays an important role in GDI injector plugging tendencies. Currently, optimized conventional synthetic gasoline deposit control additives are seen to provide excellent GDI injector keep clean performance relative to the base fuel. Beside GDI engine injector fouling, many reported results had shown that IVD and CCD fuel effects are reversed between GDI and PFI engines. Fuel additive decreased CCD under rich (below stoichiometric) and lean (above stoichiometric) engine operating cycles in GDI vehicles, particularly in the piston top bowl area, and increased IVD under rich conditions, while the reverse was observed in PFI vehicles [5].

The effects of above described deposits on engine performance are complex, different in different engines and not always harmful. For example usually CCD may improve fuel economy. Deposits in the carburettor throttle body and air bleed areas can put out of tune air/fuel ratios leading to driveability problems such as stumble, stalls and hesitation. Sometimes, in carbureted engines, intake valve deposits can be so severe as to restrict mixture flow into the combustion chamber, leading to a reduction in power. In extreme cases, deposits can even interfere with valve closing and lead to valve burning. In some sensitive PFI engines, even low levels of intake valve deposits can disturb engine performance. Cold start and warm – up driveability can be adversely affected and exhaust emissions increase. This emissions increase occurs (both HC, CO and also NO_x) because the deposits act somewhat like a sponge, alternately absorbing then releasing fuel, which upsets the delicate air/fuel ratio, particularly during transients. The change in air/fuel ratio results in excess oxygen as fuel is combusted and exhaust passes the oxygen sensor. As the excess oxygen varies, the electronic engine control system moderates the fuelling rate, since the system feedback suggests that fuelling needs adjustment. The engine tries to compensate for incorrect fuel delivery, and stumble or hesitation can result. This not only increases emissions coming out the engine but hurts the conversion efficiency of the catalytic converter as well. Deposits in the combustion chamber can cause knocking, pinging, engine run-on and octane requirement increase. The CCD act as insulators and also as heat reservoirs, storing heat in one cycle and releasing it to the fresh charge in the next cycle. They also occupy volume, increasing the compression ratio. Finally they might also absorb and release unburnt fuel, pro-knock species and promote chemical

reactions through catalytic effects [6]. Combustion chamber deposit interference is the other problems which sometimes occur in certain modern engine designs. Combustion chamber deposit interference is the result of physical contact between deposits on the piston top and cylinder head and is manifested as a loud, metallic banging sound when the engine is cold. This phenomenon is limited to the engines that have been designed, primarily to reduce emissions, with minimal clearance (about 1 millimeter or less) between some areas of the piston top and the cylinder head (squish areas) when the piston is at the top dead center. An increase in combustion chamber surface temperatures, usually brought about by increasing the coolant temperature, reduces HC emissions [6], and since CCD increase surface temperatures they might be expected to reduce HC emissions. Also, it is possible that deposit in the crevices could reduce crevice volumes which are major sources of HC emissions. So, CCD could reduce HC emissions through this mechanism [6]. Sometimes, CCD lead to improved fuel economy, as engine running on fuel containing IVD detergents and primarily CCD levels increases what lead to CO₂ emissions decrease. NO_x emission generally increases as the deposits build up. Effect of CCD on CO emission is not clear. The spark plug, located in the combustion chamber, can also suffer from excessive deposits, which can cause startability problems. At last, CCD increase the charge temperature and flame propagation rate, and reduce volumetric efficiency and the heat lost to the coolant what is reflected among other things as an reduction in maximum power.

Port fuel injection deposits form during the “hot soak” period after the engine has been turned off. The stationary gasoline trapped in the injector tip is exposed to a higher temperature for a longer time than the gasoline that flowed through injector when the engine was running. The heat degrades the gasoline and initiate deposit formation. In absence of an effective additive, injector deposits can form quite rapidly if the base gasoline is relatively unstable and if a vehicle is used predominantly for short trips. These deposits can impact on fuel flow, upsetting the air/fuel mixture and in consequence influence for hesitation or stumble during acceleration, loss of power, increased emission of hydrocarbons and carbon monoxide. In GDI engines, fuel spray pattern impact combustion quality, which if not optimal can lead to loss in power and fuel economy, as well increased exhaust emissions. Fuel composition plays an important role in GDI injector plugging tendencies. All internal injector deposits are only fuel-derived. External injector deposits appear to be primarily fuel-derived but also contain crankcase lubricant elements like: Ca, Zn, Mg, P and S. Deposit formation inside of injector orifice can both restrict fuel flow and alter the spray pattern and penetration distance. Disturbed fuel spray will tend to atomize less, penetrate deeper into the combustion chamber, and impinge on the piston surface, giving rise to less complete combustion [17]. Poor atomization can also lead to higher levels of exhaust particulates and increased levels of soot in the crankcase.

3. Development and role of deposit control additives

Gasoline additives have a long history, and their uses have gone hand in hand with developments in gasoline and automotive technology. Over the years, numerous additives have been incorporated into automotive fuels to 'improve' their properties and on-road performance features as well as helping to meet official specifications. The Fig. 10 indicates how the application areas for the different types of additives, when they began to evolve and their approximate blend concentrations.

The first important additive class was carburettor detergents consists of relatively inexpensive low-molecular weight surfactants used at low concentrations. In the 1960's, they were effective in preventing and in many cases, removing deposits from carburettor throttle bodies, but they were not effective in preventing deposits in other parts of carburettor like the air bleeds, or in the rest of the intake system. Detergent dispersants were additives of next class and consisted of polybutene succinimides. They were used at concentrations three to five times higher than carburettor

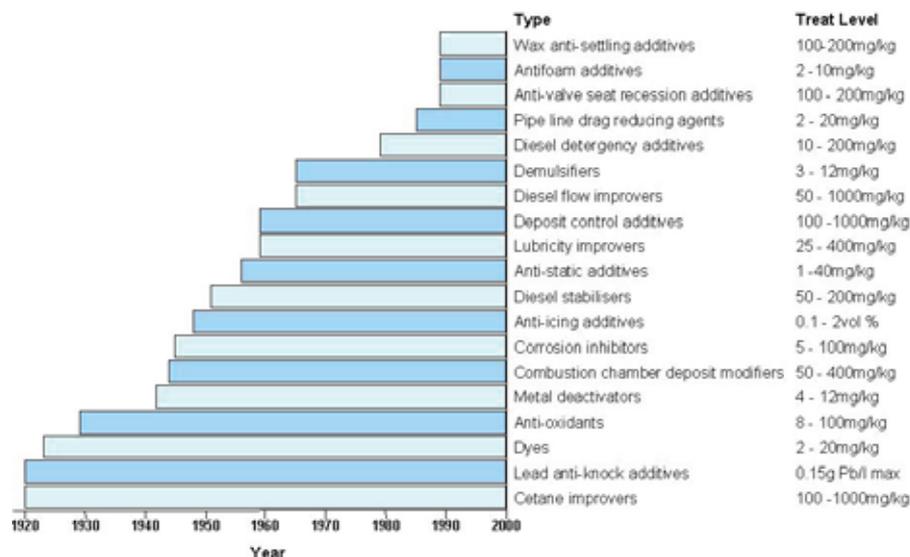


Fig. 10. Fuel additives types and history [18]

detergents and their performance was sometimes improved by using them in combination with a petroleum carrier oil. They provided keep-clean performance for the intake manifold and intake ports, but they had poor performance both in preventing intake valve deposits and carburettor as well as injector clean-up. One should be explained that can be distinguished two performance categories for deposit control additives: keep-clean and clean-up. Keep-clean indicates that when additized fuel is tested in a “clean” engine, the part of interest still will be relatively clean at the end of the test. Clean-up indicates that when additized fuel is tested in an engine where deposits have been earlier formatted on the part of interest, the deposits on the part will be significantly reduced at the end of the test. In the 1970’s had been introduced new class of additive, that means deposit control additives. It was based on polybutene amine chemistry and was used in combination with carrier oil. These class additives provide benefits throughout the engine intake system. They clean-up and keep-clean the throttle body and upper areas of the carburettor, fuel injectors, intake manifolds, intake ports and intake valves. Unfortunately when they were used in unleaded gasoline, they increased combustion chamber deposits. As have been found, some detergent additives and some carriers are more likely to increase combustion chamber deposits than others in particular engine tests [6]. In response, the second generation of deposit control additives especially for use with unleaded gasoline was developed and introduced in 1980. It was based on new polyether amine chemistry, which provides excellent control performance throughout the all intake system with small adverse side effects on combustion chamber deposits. These additives are based on fully designed chemistry intended to control combustion chamber deposits. While all the additives increased combustion chamber deposits compared to base fuel, the fully synthetic additive packages causes less of an increase than the packages formulated with a mineral oil carrier fluid.

When the fuel injector deposit problem was recognized, many oil companies adopted the use of deposit control additives. Now, the presence of deposit control additives in gasoline is critical for maintaining clean DISI injectors and for removing deposits that may have already formed. Carried over studies compared the performance of a polyether amine detergent to the Mannich detergent in a port fuel injected engine converted to DISI operation. The effects of the various different types of additives on the injectors nozzles of DISI engines shows that only additives based on polyisobutene monoamine are capable of performing well in modern engine designs incorporating gasoline direct injection technology as well as in conventional multiport-injection engines [18].

Detailed chemical composition and formulations remain proprietary to the individual additive company and normal protected by world-wide patents.

4. Test methods for evaluation of gasoline engine deposits formation

There are numerous gasoline engine deposits evaluation tests in use throughout the world which use bench engines to simulate deposit formation and detergency performance. The most widely used, generally accepted are summarized below in Tab. 2.

Tab. 2. Engine deposit tests

Test	Engine	Test description	Typical deposit	
			Base fuel	Additized fuel
CEC F-05-93	MB M102E 2.3 dm ³	60 h dyno	200-500 [mg/valve]	≤ 30 ^{**} [mg/valve]
CEC F-20-98	MB M111 2.0 dm ³	60 h dyno	300-800 [mg/cyl]	≤ 50 [mg/valve] ≤ 2500 ^{**} [mg/engine]
ASTM D 5500	BMW 318i 1.8 dm ³	16 000 km vehicle	290 ^{*)} [mg/valve]	≤ 100 ^{*)} , ≤ 50 ^{**} [mg/valve]
ASTM D 6201	FORD 2.3 dm ³	100 h dyno	300-1000 [mg/cyl]	≤ 50 ^{**} [mg/valve]
ASTM D 5598	Chrysler PFI 2.2 dm ³ Turbo	16 000 km vehicle	20-40 [% flow loss]	≤ 5 ^{**} [% flow loss]
ASTM D 6421	Chrysler PFI 2.2 dm ³ Turbo	44 h dyno	25-50 [% flow loss]	≤ 10 ^{**} [% flow loss]

^{*)} D5500 is the test required by the U.S. EPA and California ARB to certify additive performance for intake valve cleanliness. These represent the minimum acceptable base fuel result and the maximum acceptable additized result for U.S. EPA. CARB require less than 50 mg/valve additized result.

^{**}) World Wide Fuel Charter recommendation, for gasoline category 3 and 4.

Two of them has been worked up and next developed by Groups of CEC (Coordinating European Council), member of which is from many years ITN (from the 1th January of 2008 - INiG). CEC is an industry-based organisation for the development of new Test Procedures for the performance testing of Automotive Engine Oil, Fuels & Transmission Fluids (using gasoline & diesel engines). CEC represents the Automotive Fuels, Lubricants, Additives and allied industries in the development of performance tests, usually via their European Industry Groups; ACEA, ATIEL, ATC and CONCAWE. CEC Test Methods are used extensively by the automotive and petroleum industries in Europe and throughout the world.

All, described in Tab. 2 tests are recommended by World Wide Fuel Charter for evaluation of deposit formation tendency of four different gasoline categories

5. Summary

All time study is continued toward the goal of understanding deposit formation process in gasoline engines, by probing the impact of engine operating conditions and fuel compositions on the engine deposit formation. At present it is well known that deposits formed in the injectors, intake valves and combustion chambers of gasoline engines can cause various performance and emissions problems. The important factor in deposit formation is adding detergent additives in the base fuel. In majority cases the adding gasoline detergent additives in base fuel showed the strongest effects to reduce the amount of deposits. So, over past several decades, gasoline detergents have evolved to better and better control gasoline engine deposits.

Many engine tests throughout the world have been developed to asses different base gasolines as well as the influence of additives and treat rates on gasoline engine deposit formation.

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