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Advances in petrol additives research

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Abstract. A review about the use of petrol additives and the latest results in respective research and development is presented. Today it is not possible to guarantee the stable work of an engine and cleaner air by reducing the concentration of toxic compounds in exhaust gases without petrol additives. These additives control deposits, give an antiknock effect, enhance the combustion process, stabilize petrol, prevent corrosion, etc. Today it is known that the most important additives are the deposit control additives. Ethanol with a small amount of water and other additives enhance the combustion process. The improved combustion decreases fuel consumption and reduces air pollution.

Key words: petrol blends, additives, detergents, combustion improvers, antiknock agents, ethanol, water.

INTRODUCTION

In this paper a short review about the development of petrol additives research and the latest results in this field are presented. The role of additives in petrol blending is increasing. The number of respective publications, especially patents, has grown as well. The latest patents are concentrated mostly upon the deposit control or cleanliness additives, which are mainly detergents. Antiknock additives are the second largest class of objects amongst the recent patents, but the number of these patents has grown on the basis of metal (manganese, iron) compounds, which cannot be regarded as modern additives. However, it can be hoped that they have no future. Combustion catalysts and improvers have also an important role to play. Typical fuel additives are oxidation inhibitors or antoxidants, which are especially necessary for petrol containing cracking blending components. These additives prevent oxidation, polymerization, and polycondensation processes in petrol. They reduce gum formation and further

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deposit formation. Beside inhibitors, antioxidants, and stabilizers this class of additives includes inhibitors that prevent corrosion and rust formation and also metal deactivators inhibiting gum formation catalysed by some metals. These additives are mostly phenol or amine derivatives. Among the recent patents in this field, there are not any new groups of chemical compounds.

In 2002, of the published patents and patent applications 57% described deposit control additives, 26% antiknock agents, 5% combustion improvers, 5% water stabilizers in petrol, 3% antioxidants, inhibitors, stabilizers, and others (emission reducing additives, antiwear agents, de-emulsifiers, etc.). The modern additives are complex mixtures containing many ingredients. The content of hydrocarbons (mainly alkenes and aromatics) and also oxygenates (methyl *tert*-butyl ether, ethanol, etc.) in petrol determines the type and amount of additives to be used. Some of the additives have often many functions, for instance deposit control and inhibition, deposit control and combustion improvement, deposit control and antiwear function, etc.

In the petrol additives research some reviews have been published earlier [1–10]. Taking into consideration the new trends and problems in this research field a short review about deposit control additives, antiknock agents, combustion improvers, and problems concerning the water content in petrol is presented here.

DEPOSIT CONTROL ADDITIVES

Deposit control additives are petrol soluble detergents, which must be compatible with the lubricating oil. The detergents hinder the formation of deposits. They also enter into the deposit particle to remove it from the inner surface of the engine and disperse it into fuel. The effect is based on the decrease of the surface tension. Three major areas of engine deposits are the fuel metering system (carburettor and fuel injectors), the induction system (manifold, intake ports, and intake valves), and the combustion chamber (piston top and cylinder head area) [1]. In 1954 Chevron Co. was the first to introduce petrol detergents to keep the carburettors or fuel injectors clean. These additives are usually low molecular weight amines and amine carboxylates, which compete with deposit precursors and also help to disperse deposits. High molecular weight polybutene amines developed by Chevron Co. in 1970 control deposits on intake valves, manifolds, and ports. In this field polybutene amines were joined with polyether amines [2]. Combustion chamber deposits cause also the knock effect, decreasing thus the octane value. Deposit control agents in the combustion chamber are compounds with high temperature stability, mainly succinimide derivatives [3, 4].

A review about nitrogen compounds as intake valve and combustion chamber deposits control additives was published by Sakulpaisith [5]. Polyether amines, polyisobutylene amines, and polyisobutylene succinimides as fuel additives reduce the intake valve deposit by 45–60% from the base fuel and lower somewhat the combustion chamber deposit when compared to the base fuel. Combustion chamber deposits cause an increase in the octane number requirement or an

“octane appetite” or ORI (octane number increase) is greater. The combustion chamber deposit control additives are also called anti-ORI additives. Deposits in the combustion chamber increase the temperature therein. The higher temperature causes a growing formation of nitrogen oxides from nitrogen and oxygen in the emission. All types of engine deposits increase fuel consumption and exhaust emissions (carbon monoxide, hydrocarbons, and nitrogen oxides). A clean engine means cleaner air. Modern additives do not only hinder deposit formation but also clean the engine up. Advances in engine and also fuel technology reduce the possibilities of deposit formation, but do not stop their formation in the engine. Some vehicles are very sensitive to deposits while others are not. The composition of petrol hydrocarbons affects deposit formation.

Alkenes and especially alkadienes as well as compounds with heteroatom play an important role in the forming of deposits. In modern petrol blending alkadienes are eliminated. Alkenes from catalytic cracking streams form deposits in the introduction system, especially in the intake ports and valves. The alkenes content in European petrol is up to 18%, in the United States it is in the range 6.0–9.5%. The alkenes content in modern petrol and engine oil are the main factors causing the formation of engine deposits [6]. Aromatic hydrocarbons, especially the higher boiling compounds (cumene, isobutyl benzene, etc.), are the major factor in base fuel that affect combustion chamber deposits. These components are found in reformats and also in cracking streams. Aromatic hydrocarbons content in European petrol is up to 42% and in the United States 20–25%.

The best components in petrol blends are alkylates and isomerisates. The production of alkylates forms in Europe approximately 5% and in the United States approximately 12% of petrol blending components. The production of isomerisates is approximately 5% of all petrol blending streams both in Europe and the USA. Thermally stabile polyalkylene polyamines were synthesized at first from poly-isobutene chloro derivatives and the corresponding amine. The residues from the production of these products are dangerous for the environment. These additives can also contain traces of chlorine compounds, which cause corrosion in the engine. Chlorine free polyetheramines are of better value. They are synthesized from alcohols by oxyalkylation. After that the hydroxyl group is cyanethylated and finally the obtained nitrile is reduced to amine [11–13].

Lubrizol Corp. patented an effective aromatic amide as a fuel intake system deposit control agent in 1994. These amides contain hydroxy, alkoxy, and other polar groups [14].

A novel class of petrol detergents, polyether hydroxyethylaminoethyl oxalamides, was patented by Texaco Inc. [15]. The additives that control the combustion chamber deposits must be thermally stabile. Alkenylsuccinimides obtained from succinic anhydride and amine, polyalkenylamine or its oxyalkyl derivative are effective. Succinimides are also used as intake valve deposits control additives [4, 16, 17]. The petrol detergency additives based on bisalkenyl-succinic acid imides were patented, and it was shown that the efficiency of these compounds increases with increasing nitrogen content in the molecule [18].

Texaco patented a novel class of asymmetric urea derivatives of either hydrocarboxyloxypolyether amine alone, or a hydroxyloxypolyether amine and a tertiary aminoalkyl primary amine [19]. The reaction products of 4-alkyl-2-morpholinone with an alkylphenoxypolyoxyalkylene amine together with polyethenepolyamine succinic acid anhydride derivatives and polyalkenes as fuel detergent additives are also interesting [20].

A large number of deposit control additives are amines. Oligomeric alkene monoamine for instance was prepared by epoxidizing an oligomeric alkene to form an oligomeric alkene aldehyde and an oligomeric alkene monoamine, which is obtained over oxime. This method gives a chlorine free product [21]. Hydrocarbyl-substituted polyoxyalkene amines [22], polyether amines [23], esteramines [24], and polyisobutene amines, hydrazines, and azides [25] are also patented. From nitrogen compounds amides (for instance alkoxylated poly(oxyalkylene)triamides [26], polyether alcohol monoamides [27], alkanolamides comprising an alkoxylated urea, etc. [28]) also play a great role in deposit control. Guanidine, urea, or thiourea substituted carboxylic acids or their salts as deposit control agents also reduce wear [29].

In the large group of succinic acid derivatives an effective additive was lately patented by Lubrizol Corp. [30]. It must be repeated that it is very essential to synthesize the nitrogen containing additives without a step over halogen containing compounds. An interesting way was presented by Kinder et al. [21].

Carbamine acid derivatives are also detergent additives for deposit control [31]. An interesting group of deposit control agents can be obtained by the Mannich condensation; these are so-called Mannich compounds [32–39]. The aldehyde or ketone compound in the Mannich reaction can derive from a polyalkene, especially polyisobutene, also an amine compound [33]. High molecular weight Mannich condensates prevent also the clogging of engine oil [32]. A wide set of nitrogen compounds, Mannich amines, polyalkenyl succinimides, polyalkylene carbamates are patented by Shell Oil Co. [35].

Other nitrogen compounds are patented as fuel additives as well, for instance, polyalkylpyrrolidines and fuel soluble salts thereof having an average molecular mass in the range of 500 to 5000 [40]. Methacrylate polymer containing primary amino group reduces deposits [41].

Poly(oxyalkylene)pyridyl and piperidyl ethers [42] and pyridyl and piperidyl esters of polyalkylphenoxyalkanols control deposits in engine [43].

The patenting of new ether compounds as deposit, especially intake valve deposit, control additives continues [44, 45]. Ether derived from tetrahydrofuranylmethanol or polytetrahydrofuran is also a petrol detergent additive [46, 47]. Carboxylic acid alkoxylates together with polybutene amines act in a similar manner [48].

Potassium, sodium, calcium, and other metal salts of aminophenol carboxylic acid derivatives prevent the formation of deposits. They also are catalysts of petrol combustion [49].

It is interesting to note that elemental phosphorous or amine salt of a phosphorous based acid in the mixture with ferrocene is patented as a valve seat deposit control agent [50, 51]. On the other hand it is known that ferrocene can cause deposits.

It was shown that some flakes of combustion chamber deposits are hydrophilic and water is far more effective to take these away than petrol or other organic solvents [10]. This indicates that a small water content in fuel reduces the amount of deposits. Lubrizol Corp. patented a copolymer of alkenes and maleic anhydride, which is effective in producing a stable and clear aqueous fuel emulsion [52]. Ethanol in this case plays also a positive role [53]. It may be possible to clean the engine and exhaust gases when seawater components are added to petrol [54]. Corrosion problems, however, arise here.

The following is a list of the most essential patents and patent applications about deposit control additives published in 2002: polyisobutenylphenols [55], phenol alkylated by polyisobutene and after that propoxylated [56], alkoxylated fatty amines [57], hydroalkyl- and aminoalkyl-terminated polyoxyalkenes [58], poly(oxyalkene)amine and aromatic esters [59], polyoxyalkene aminoalcohol [60], amidoamine-terminated polyoxyalkene [61], hydrocarbyl compounds [62], and oleic alkanolamide and alkoxylated oleic acid [63]. Succinic derivatives, which were synthesized unfortunately over halogen compounds, were also patented [64]. Deposit control amine and other nitrogen compounds can also have inhibiting and stabilizing properties.

ANTIKNOCK ADDITIVES

Tetraethyl lead has been added to petrol since the 1930s as an effective antiknock and also antiwear additive. In 1996 it was totally banned in the USA and replaced by methyl *tert*-butyl ether [65]. In Europe leaded petrol is not absolutely forbidden although in the standards the maximum lead content allowed in petrol is 0.005 g/L [66]. Lead is a hazardous neurotoxin. On the other hand, the elimination of lead compounds from petrol would cause the wear of the engine, especially of the exhaust valve seat, due to a lack of local lubrication. This problem has been resolved by alkali metal based anti-valve seat recession additive technology. Additive compounds containing alkali metals, especially potassium, are used for instance in Austria already since 1990. Germany and also Estonia were mentioned by Wilkes [67] as countries where unleaded petrol containing alkali metal based anti-valve seat recession technology is partially applied. In connection with the toxicity of tetraethyl lead new agents to reduce the antiknock effect were patented already in the 1980s. It was shown that molybdenum compounds are not only lubricating oils with antiwear additives, but they also act as petrol antiknock agents [68]. Also tri-, tetra-, and pentaethyl bismuth are patented as nontoxic antiknock additives [69]. Iron compounds, so-called ferrocenes, are used as antiknock agents, but they form deposits in the engine. Methylcyclopentadienyl manganese tricarbonyl (MMT) and other

manganese compounds have been used to enhance the octane value of petrol, but they are toxic [70]. In spite of their unsuitability as antiknock additives, iron [71, 72] and manganese compounds [73, 74] are described for this purpose in many patents. To call ferrocene and similar fuel additives as modern [75] in 1998 is slightly strange.

It is highly probable that the widely used effective antiknock additive methyl *tert*-butyl ether (MTBE) will be replaced by ethanol [76]. There are also many other suggestions to replace the toxic MTBE, for instance by dimer of isobutene [77]. This case is doubtful because the octane number of isobutene dimer is approximately the same as that of isooctane and it is not very stable. 1,3-Diaminopropane enhances the ignition quality if 3.0–5.0% is added to petrol and it performs better than MTBE [78]. However, this compound probably increases the nitrogen oxides content in emissions. 2,3-Dimethyl-2-methoxybutane can replace effectively MTBE. Its solubility in water and its toxicity are very low [79], but its price is supposedly higher than that of MTBE. Dimethyl carbonate is patented as an antiknock additive [80]. Oligomers of C_2–C_5 alkenes etherificated with methanol or ethanol have low water solubility and they can replace MTBE [81]. A paper about lithium organic compounds as antiknock additives was published by Mavrin et al. [82]. It is interesting that high-molecular polyalkenes (e.g. polyisobutene, molecular mass 20 000–9 000 000) with detergents and other additives are patented by BASF as octane number increasing agents [83]. It was shown by Flynn et al. [84] that 1,3-dioxolane has the ability to be an effective oxygenate for reformulated petrol and its blending costs are equivalent to those of ethanol.

COMBUSTION IMPROVERS

Combustion improvers include combustion catalysts and ignition promoters. Alkali or alkali earth metal compounds in which, for instance, the anion is a polymeric sulphonated phenol [85] are patented as deposit control agents. These alkali metal compounds are undoubtedly also combustion improvers. Combustion catalysts are commonly alkali or other metal salts and they are used in ppm concentrations. A list of the essential patents of combustion catalysts will be presented. Iron and cerium enolates in a concentration of 3–200 ppm are patented as combustion improving additives [86]. Many metallic compounds that do not dissolve in petrol and are in the form of dispersion have been patented: chromium-, magnesium-, manganese-, and cobalt oxides [87]; tetravalent cerium oxide [88]; selected from IIA and IIB group metal oxides, hydroxides, and peroxides [89]; potassium molybdate [90]; noble metals and rhenium complexes [91]. Unsoluble compounds can cause deposits in engine. It is better when the combustion catalyst is soluble in petrol.

Aromatic sulphonates, phenates, and salicylates of magnesium, calcium, and barium as combustion enhancers are described [92]. The most essential compounds as fuel catalysts are alkali or alkali earth metal derivatives, especially potassium salts of organic acids soluble in petrol. Of potassium or sodium compounds the

former with a better solubility are more effective. The combustion end products of these compounds are carbonates.

Next some alkali and alkali earth metal derivatives as petrol additives will be described. Succinic acid derivatives were patented by Shell Oil Co. already in 1987 [93, 94]. It was shown that alkali metal salt of a partial ester of an alkyl polyether alcohol is a spark aider and anti-valve stick agent in petrol compositions [95]. By improving the combustion process, the accompanying deposit formation can be diminished. The salts of sulphosuccinic acid esters are enhancers of petrol combustion [96]. Dioctylsulphosuccinate potassium salt and the detergent polybutene amine are patented as antiwear additives [97]. The potassium salt is surely a combustion improver and polybutene amine acts as a deposit control agent. Alkali naphthenates are also combustion enhancers in petrol [98, 99]. Potassium salt of dodecyl naphthalene sulphonic acid as a petrol additive reduces also wear in the engine [99]. Bratsky et al. [49] patented potassium salts as detergents to reduce deposits, and these are also combustion enhancers. Some petrol soluble potassium salts of organic acids or phenolates are unstable in petrol ethanol blends. Therefore Orr [100] patented stable salts, especially potassium phosphates, as combustion enhancers in petrol ethanol blends. In our investigation it was also shown that salts stable in petrol ethanol blends act as combustion catalysts [101]. A patent was lately published where it was shown that hydroxylamine salts are combustion improvers [102]. Potassium salts as petrol additives are not only combustion catalysts but also antiwear agents. It was shown [67] that at potassium levels in the fuel above 5 ppm wt/wt, valve seat recession is halted completely within 10 hours of treatment. The "memory effect" (which exists when lead compounds are used) was also found to be longer when a higher fuel potassium concentration was used.

Compounds that can be classified as combustion supporters but not as catalysts, for instance nitroalkanes, have been patented [103, 104]. In these patents it is noted that nitroalkanes as petrol additives reduce nitrogen oxides emissions. Generally, reducing nitrogen oxides content in exhaust gases is connected with reducing the combustion temperature in the combustion chamber. It was not clear whether the nitroalkanes reduce the combustion temperature or not. Usually nitrogen compounds in petrol increase the nitrogen oxides emission. Ethylacetate as a petrol additive to improve combustion is patented as well [105]. Ethylacetate may be interpreted as an oxygenate. Oxygen in oxygenates supports combustion. Alcohols and ethers and also aldehydes as oxygenates added to petrol decrease the carbon monoxide and hydrocarbons content in emission and improve combustion [106]. But the instability of aldehydes can be an obstruction to their use as oxygenates.

WATER IN PETROL

Water is usually regarded as an unsuitable component in petrol. As hydrocarbons are very hydrophobic compounds there are no problems with the water

content in the hydrocarbonic petrol at all. The hydrophilic oxygenate additives such as ethanol in petrol blends can promote the increase of water content in these mixtures. It was demonstrated that a low water content in petrol reduces the concentration of toxic compounds (CO, NOx) in motor emissions. It is also useful for powering spark ignition engines [107, 108]. Water in petrol decreases the calorific value of the motor fuel but a low concentration of water improves the combustion process in the engine. The problem is to stabilize the water and petrol blends. There are many patents since 1971 concerning the stabilization of water in petrol. Acetals and alcohols as fuel additives improve the octane number value and also increase the water tolerance of petrol [109]. A small amount of submicron structured water added to ethanol and blended then with petrol enhances the combustion process [110]. The same effect is obtained also with ordinary water. It was shown by Bertha [111] that C_5–C_{10} and carboxylic amides C_5–C_{10} as additives stabilize the water content by 10–40% in hydrocarbon fuel. It must be mentioned that the water content in fuel as high as 40% cannot influence positively the combustion process. The same can be noted about the patent by Wenzel [112] in which the water content in petrol was up to 36% and it was stabilized by alcohols, ethoxylated alcohols, fatty acids, or ethanolamines. The stabilizer concentration must be very high to inhibit the water separation from petrol blends containing 36 or 40% of water.

The vapour pressure of petrol and alcohol blend can be reduced by adding a surfactant compound comprising an alkanolamide, e.g. lauryl diethanolamide, alcoxylated alcohol, and alkoxylated fatty acid [113]. These additives can also stabilize water in petrol. Demirbas [114] found that C_3–C_5 alcohols are the most effective blending agents in reducing phase separation in methanol or ethanol, petrol, and water blends. In our investigation [101] it was shown that petrol and ethanol blend with a low water content, hydrophilic potassium combustion catalyst (0.1–200 ppm), and a detergent additive is a stable clear liquid, which enables to decrease essentially the toxic components in emission and also deposits in the engine. Fuel compositions comprising alcohol, petrol, and water converting this hazy or potentially hazy blend into a clear and stable solution by adding anionic surfactant of an aminated polyisopropoxylated, polyethoxylated alkylphenol have been patented by Texaco Inc. [115]. Polyisobutenamines known as deposit control additives are suitable emulsifiers for water and petrol blends [54, 116]. A water and ethanol containing petrol blend that contains furfuryl alcohol and ethene oxide is patented [117], but it must be mentioned that these additives are relatively unstable. Many surfactants have been patented for stabilizing alcohol, petrol, and water blends (for instance 118–120).

CONCLUSIONS

Additives play a key role in the modern petrol blends. Deposit control, antiknock, antioxidant, combustion improver, and all additives in the class of inhibitors are the most important agents to reduce the fuel consumption and

concentration of toxic compounds in engine exhaust gases. These additives guarantee the stable work and prolong the age of the engine. It is very essential to combine the combustion catalysts with deposit control additives. The modern additives are combined from many agents and are multifunctional. Ethanol as an octane number and combustion improver with a small amount of stabilized water in the petrol blend enhances the combustion and reduces the toxic components concentration in emissions.

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REFERENCES

1. Ter Rele, R. R. J. & Peyla, R. J. Deposit control additives for future gasolines – a global perspective. *Petr. Coal*, 1999, **41**, 1, 3–19.
2. Peyla, R. J. Additives to have key role in new gasoline era. *Oil Gas J.*, 1991, **89**(6), 53–57.
3. Gibbs, L. M. Gasoline additives – when and why. *Soc. Automot. Eng.*, 1991, 902 104.
4. Herbstman, S., Kaufman, B. J., Bitting, W. H. & Choate, P. J. (Texaco Inc.). Gasoline detergent additive mixture of mono- and bis-succinimide and heavy oil. US 5 256 195, 1993.
5. Sakulpaisith, N., Wuttimongkolchai, A. & Sretainind, T. Vehicles fleet test. *Soc. Automot. Eng.* SP-1563, 2000, 1–5.
6. Ansomboon, J., Wuttimongkolchai, A., Pannoi, S. & Fukuda, K. Characterization of deposits and effects of detergent additives. *Soc. Automot. Eng.* SP-1563, 2000, 7–14.
7. Danilov, A. M. New additives for fuels. *Khim. Tekhnol. Topliv. Masel*, 1998, 1, 35–38 (in Russian).
8. Danilov, A. M. *Additives and Additions*. Moskva, 1996 (in Russian).
9. Noels, A. F. Les carburants modernes pour l´automobile. *Chim. Nouv.*, 2000, **18**, 3191–3194.
10. Kalghatagi, G. T. & Price, R. J. Combustion chamber deposit flaking. *Soc. Automot. Eng.* SP-1563, 2000, 29–40.
11. Cherpeck, R. E. (Chevron Co.). Poly(oxyaklylene)hydroxyaromatic esters and fuel compositions containing the same. PCT WO 94/14926, 1994.
12. Cherpeck, R. E. (Chevron Co.). Fuel additive compositions containing poly(oxyalkylene) hydroxyaromatic ethers and poly(oxyalkylene)amines. PCT WO 94/14927, 1994.
13. Lin, J. J., Macias, J. R., Haury, E. J., Weaver, S. L., Edwards, C. J., Wang, P. C. & Vaporiciyan, G. L. (Shell Oil Co.). Fuel composition with cyclic amide alkoxylated compounds as additives. US 5 352 251, 1994.
14. Adams, P. E., Lange, R. M. & Stoldt, S. H. (Lubrizol Corp.). Fuel composition containing an aromatic amide detergent. US 5 336 278, 1994.
15. Su, W. Y., Herbstman, S., Zimmerman, R. L. & Cuscurida, M. (Texaco Inc.). Polyether hydroxyethylaminoethyl oxalamides as motor fuel detergent/dispersant additives. US 5 286 267, 1994.
16. Sung, R. L. (Texaco Inc.). ORI-inhibited motor fuel composition and storage stable concentrate. US 5 061 291, 1991.
17. Powers, W. J., Mathews, L. A., Leong, M. F. & Erickson, R. W. (Texaco Inc.). Process for producing ORI control additives. US 5 147 414, 1992.
18. Thielbeule, W. & Finmans, P. Kraftstoff-Additive für Otto-Motoren und Kraftstoffe, die diese enthalten. DE 4 234 032, 1994.
19. Herbstman, S. (Texaco Inc.). Motor fuel detergent additives – asymmetrical ureas of hydroxycarboxy polyether amines and tertiary aminoalkyl primary amines. US 5 286 266, 1944.

20. Russo, J. M., Herbstman, S. & Furman, J. B. (Texaco Inc.). Gasoline detergent additive composition and fuel composition. US 5 286 264, 1994.
21. Kinder, J. D., Baldwin, L. J., Dever, J. L. & Sonby, K. Production of halogen-free oligomeric olefin monoamines used as fuel additives. US 6 303 703, 2001.
22. Morris, J. E., Moore, S. M. & Sabourin, E. T. (Chevron Chem. Co.). Fuel composition containing hydrocarbyl-substituted polyoxyalkylene amines. PCT WO 00/49109, 2000.
23. Arters, D., Daly, D. T. & Jackson, M. M. (Lubrizol Corp.). Fuel additives containing amine used in fuel composition for reducing valve deposits. US 6 193 767, 2001.
24. Kanakia, M. D., Franklin, R., Steichen, D. & Gadberry, J. M. Fuel additive compositions for simultaneously reducing intake valve and combustion chamber deposits. US 6 013 115, 2000.
25. Courtier, J. L., Kervennal, J., Germanaud, L. & Maldonado, P. Amine, hydrazine, and azide derivatives of polyisobutylenes, their production and their use as detergents in fuels. PCT WO 00/32650, 2000.
26. Lin, J., Su, I., Lin, K., Ho, Y., Lee, C., Shin, W. & Ku, W. Star-like poly(oxyalkylene)triamide alkoxylates gasoline additive and the method for producing the same. US 6 270 540, 2001.
27. Lin, J. J., Macias, J. R. & Weaver, L. (Shell Oil Co.). Fuel compositions. US 6 312 481, 2001.
28. Rae, A. Fuel additives. PCT WO 01/44413, 2001.
29. McDonnell, T. F. & Rollin, A. J. (Ethyl Corp.). Fuels with enhanced lubricity. EP 1 013 746, 2000.
30. Daly, D. T., Adams, P. E. & Jackson, M. M. (Lubrizol Corp.). Additive composition. US 6 224 642, 2001.
31. Kendall, D. R. (Shell Oil Co.). Additive concentrate for gasoline engine. PCT WO 01/32812, 2001.
32. Ahmadi, M. R. & Morris, J. E. (Chevron Co.). Fuel additive composition containing Mannich product and hydrocarbon substituted polyoxyalkylene amines. EP 1 193 308, 2002.
33. McAtee, R. J. (Lubrizol Corp.). Polyalkenylphenol-derived aromatic Mannich compounds as diesel fuel and gasoline detergents. PCT WO 00/78898, 2000.
34. Aradi, A. A. & Colucci, W. J. (Ethyl Corp.). Fuel composition for direct injection gasoline engines containing Mannich detergents. PCT WO 01/42399, 2001.
35. Graham, J., Aiello, R. P. & Haury, E. J. (Shell Oil Co.). Additive concentrates for rapidly reducing octane requirement in gasoline. US 6 261 327, 2001.
36. Puri, S. K., Gupta, A. A. & Rajesh, M. Mannich bases prepared from hydrogenated distilled nutshell liquid as gasoline detergents and deposit inhibitors. US 2002066225, 2002.
37. Malfer, D. J., Noble, A. T., Colucci, W. J. & Sheets, R. (Ethyl Corp.). Mannich bases prepared from secondary amines disubstituted hydroxyaromatic compounds as gasoline intake valve deposit inhibitors. EP 1 229 100, 2002.
38. Houser, K. R. (Chevron Co.). Fuel additive composition containing a Mannich condensate product, a poly(oxyalkylene)monol, a polyolefin, and a carboxylic acid. EP 1 193 307, 2002.
39. Ahmadi, M. R., Gray, J. A. & Sengers, P. M. (Chevron Co.). Fuel additive composition containing a Mannich condensation product, a poly(oxyalkylene)monol, and carboxylic acid. EP 1 193 308, 2002.
40. Cherpeck, R. E. & Kramer, J. D. (Chevron Co.). Polyalkylpyrrolidines and fuel compositions containing the same. US 6 033 446, 2000.
41. Kishida, M. & Ota, Y. Fuel oil additive and fuel oil composition. JP 2001040377, 2001. C.A. 134: 165469.
42. Cherpeck, R. E. Poly(oxyalkylene)pyridyl and piperidyl ethers as deposit inhibitors for gasoline and diesel engines. EP 1 057 880, 2000.
43. Nelson, K. D. (Chevron Co.). Pyridyl and piperidyl esters of polyalkylphenoxyalkanols as hydrocarbon fuel additives. US 5 942 014, 1999.
44. Günther, W., Oppenländer, K., Schwahn, H. & Trötsch-Schaller, I. Fuel compositions containing propoxylates. PCT WO 00/02978, 2000.
45. Delford, B., Joly, S., Lacome, T., Gateau, P. & Paille, F. Isosorbide derivatives useful as detergent additives for gasoline. EP 1 106 616, 2001.
46. Delford, B., Joly, S., Lacome, T. & Gateau, P. Polyoxyalkylene ethers with tetrahydrofuranyl-methanol as gasoline detergent additives. EP 1 076 086, 2001.

47. Delford, B., Joly, S., Lacome, T. & Gateau, P. Polyoxyalkylene-terminated polytetrahydrofuran as gasoline detergents. EP 1 076 072, 2001.
48. Su, W.-Y. Fuel additives with carboxylic alkoxylates for internal combustion. US 6 210 452, 2001.
49. Bratsky, D., Oravkin, J., Zathoukal, Z., Feher, P. & Mikula, O. Prisada do automobilovych benzinov. CS 277 200, 1992.
50. Mulqueen, S. C., Vincent, M. & Cook, S. L. Fuel additive for the prevention of valve seat recession. PCT WO 01/016257, 2001.
51. Mulqueen, S. C., Vincent, M. & Cook, S. L. Phosphorous-iron-based valve seat recession additives for unleaded gasoline. GB 2 347 433, 2000.
52. Thompson, L. R. & Barr, D. M. (Lubrizol Corp.). Emulsifier for an aqueous hydrocarbon fuel. US 20010020344, 2001.
53. Hazel, C. J. & Williamson, I. V. Additive composition for fuel mixtures with alcohols. PCT WO 01/10982, 2001.
54. Nasu, A. Fuel additives. EP 394 715, 1990.
55. Lange, A. & Rath, H. P. (BASF AG). Verfahren zur Hersteelung von Polyisobutenylphenolen. PCT WO 02/026840, 2002.
56. Lange, A., Rath, H. P. & Walter, M. (BASF AG). Alkoxylierte Alkylphenole und deren Verwendung in Kraft- und Schmierstoffen. DE 10102913, 2002.
57. Jackson, M. M. & Corkwell, K. C. (Lubrizol Corp.). Gasoline additive concentrate composition and fuel composition and method thereof. PCT WO 02/079353, 2002.
58. Derosa, T. F., Russo, J. M., Kaufman, B. J., Ketcham, J. R., Kessler, R. V. & Deblase, F. J. (Texaco Inc.). Hydroalkyl- and aminoalkyl-terminated random and block polyalkenes as deposit inhibitors for automotive fuels. US 6 372 000, 2002.
59. Ahmadi, M. (Chevron Co). Polyalkenylphenyl esters with substituted benzoates as deposit inhibitors for gasoline engine. EP 1 236 789, 2002.
60. Derosa, T. F., Burns, J. M., Kaufman, B. J., Bacchi, R. J., Cryvoff, S. A. & Ketcham, J. R. (Texaco Inc.). Two-cycle engine fuel composition including a polyoxyalkylene aminoalcohol as a deposit inhibitor. US 6 346 128, 2002.
61. Lin, J. J., Ku, W. S. & Lee, C. N. Amidoamine-terminated polyoxyalkylenes as gasoline detergents and octane requirement reducing agents. US 6 454 818, 2002.
62. Cooney, A. M., Sneddon, A. T. & Trainor, J. M. Composition. PCT WO 02/022765, 2002.
63. AAE Techn. Int. Ltd. Fuel additives in fuel composition engine. EP 1 227 143, 2002.
64. Nelson, A. R., Nelson, M. L. & Nelson, O. L. Reaction products of functionalized hydrocarbon polymers with polyamines and polyoxyalkylenes as engine deposit inhibitors for gasoline. US 20020023383, 2002.
65. Reisinger, H. J. & Reid, J. B. Methyl-tertiary butyl ether natural attenuation case studies. *Soil. Sedim. Contam*., 2001, **10**, 41–43.
66. EVS-EN 228:2002. *Riigi Teataja Lisa*, 66, 30.05.2001.
67. Wilkes, M. F. (Lubrizol Ltd.). Lead replacement – European experiences. *Petr. Coal*, 2000, **42**(3–4), 161–165.
68. West, C. T. & Basalay, R. J. Hydrocarbon-soluble polyamine-molybdenum compositions. EP 49094, 1982.
69. Falkenstein, K. Anderes ungiftiges Antiklopfmittel für den Kraftstoff Benzin. DE 3 840 069, 1990.
70. Zayed, J. Use of MMT in Canadian gasoline: health and environment issues. *Am. J. Ind. Med.*, 2001, **39**(4), 426–433.
71. Wuntke, K., Zobel, G. & Hopp, W. Vergaserkraftstoffe, enthaltend Eisenacetylacetonat und Eisenpentacarbonyl. CH 689 623, 1999.
72. Szememyei, D. P. & Scriven, T. H. Fuel composition having a negative fuel sensitivity. EP 1 154 009, 2001.
73. Aradi, A. A., Roos, J. W., Scull, H. M. & Meffert, M. Fuels compositions for direct injection gasoline engines containing manganese compounds. PCT WO 01/042399, 2001.
74. Henderson, D. M. Unleaded gasoline with additives. US 6 238 446, 2001.

75. Sachivko, A. V., Tverdokhlebov, V. P., Demyanenko, E. A. & Polyakov, B. V. New additives for motor fuels. *Ross. Khim. Zh.*, 1998, **42**(1–2), 176–186 (in Russian).
76. Rang, H. & Kann, J. Recent advances in bioethanol research. 1. Bioethanol, methyl tert-butyl ether, and other oxygenates in petrol blends. *Proc. Estonian Acad. Sci. Chem*., 2003, **52**, 3–19.
77. Kolah, A. K., Zhiwen, Q. & Mahajani, S. M. Dimerized isobutene: an alternative to MTBE. *Chem. Innovation*, 2001, **31**(3), 15–21.
78. Gouli, S., Serdari, A., Stournas, S. & Lois, E. Transportation fuel substitutes derived from biomass. *J. Energy Res. Techn*., 2001, **123**, 1, 39–43.
79. Liu, J., Wang, S. & Guin, J. S. Etherification of dimethylbutenes in excess of methanol. *Fuel Proc. Technol.*, 2001, **69**(3), 205–219.
80. Komiya, K. & Tomoyasu, K. Dimethyl carbonate composition for refining of gasoline fuels for internal combustion engines. JP 2002073474, 2002. C.A. 133: 283942.
81. Wristers, J. P. & Hendriksen, D. E. Ethers with low water solubility used in liquid fuels. PCT WO 00/19771, 2000.
82. Mavrin, V. Yu., Krasnoperov, V. A., Kovalenko, A. P., Kozin, V. G. & Gavrilov, V. I. Suitability of hydrocarbon fuels for lithium containing antiknock agents. *Khim. Tekhnol. Topliv. Masel*, 2001, 6, 27–28 (in Russian).
83. Schwahn, H., Posselt, D., Schmidt, H., Mach, H., Rath, H. P. & Hüffer, S. (BASF AG). Otto-kraftstoffadditivzusammensetzung zur Erhöhung der Motoroktanzahl. DE 10109260, 2002.
84. Flynn, P. J., Ityokumbul, M. T. & Bochman, A. L. Preliminary investigation on the viability of 1,3–dioxolane as an alternative to MTBE in reformulated gasoline. *Soc. Automot. Eng*. SP-1647, 2001, 175–185.
85. Stoldt, S. H. (Lubrizol Corp.). Fuel composition. PCT WO 89/07126, 1989.
86. McKenzie, I. M., Vogel, A. M., Heiser, J. & Kenneth, W. Combustion fuel additives comprising metal enolates. US 4 474 580, 1984.
87. Lloyd, L. Fuel combustion enhancing catalytic composition and methods of formulating and utilizing same. US 5 823 758, 1998.
88. Birchem, T. & Blanchard, G. (Rhodia Chim.). Composition based on an organic sol of tetravalent oxide and an organic alkaline earth compound. PCT WO 99/13026, 1999.
89. Sanders, J. K. & Tock, R. Combustion catalyst and catalysed fuels enhanced combustion efficiency and milage. PCT WO 99/21941, 1999.
90. Kim, J. C. & Kim, S. J. Fuel additive for accelerating combustion. KR 200105434, 2001.
91. Shustorovich, A., Shustorovich, E., Montano, R., Solntsev, K. & Buslaev, Y. Gasoline additives for catalytic control of emissions from combustion engines. US 6 152 972, 2000.
92. Yoshida, E., Nomura, H. & Satoh, S. Gasoline compositions for automotive vehicles. EP 192 323, 1986.
93. Van Es, C., Miles, R., Kalghatagi, G. T., McArragher, J. S. & Heidwey, R. F. (Shell Oil Co.). Gasoline composition. EP 207 560, 1987.
94. Miles, R. & Graiff, L. B. (Shell Oil Co.). Gasoline composition. EP 290 088, 1988.
95. Van Es, C. (Shell Oil Co.). Gasoline composition. EP 491 439, 1992.
96. Henzi, U. Gasoline composition. PCT WO 91/07477, 1991.
97. Buschbaum, A. & Koliander, W. Additive for lead-free gasoline. EP 639 632, 1995.
98. Buschbaum, A. & Koliander, W. Verfahren zur Herstellung der Alkalimetallkomponenten eines Additives sowie dessen Verwendung. AT 397 659, 1994.
99. ÖMV AG. Additive für unverbleite Ottokraftstoffe auf der Basis von Alkalimetallsalzen von Alkylnaphtalinsulfonsäuren. AT 405 182, 1999.
100. Orr, W. C. Fuel composition employing as catalyst combustion structure. PCT WO 99/66009, 1999.
101. Rang, H., Kann, J. & Kriis, J. A motor fuel composition. EE 200100457, 2001.
102. Baker, M. R., Barr, D. M. & Daly, D. T. (Lubrizol Corp.). Hydroxylamines and hydroxyl-amine salts as combustion improvers for liquid biomass-derived and hydrocarbon-based fuels. PCT WO 02/065870, 2002.
103. Gonzalez, F. Chemical clean combustion promoter compositions for liquid fuels in compression ignition engines and spark ignition engines. US 5 433 756, 1995.

104. Foote, A. R. & Lakin, M. Fuel additive formulation and method of using same. US 6 319 294, 2001.
105. Lai, Z.-R. Benzin- und Diesel-Zusatz. DE 19918764, 2001.
106. Kief, H. Glyoxal in wässriger Lösung als Additiv zur Schadstoffemissionssenkung bei fossiler Brennstoffen. DE 19843380, 2000.
107. Magnin, C., Prudhomme, J. B. & Schulz, P. Method and apparatus for preparing an emulsified fuel. PCT WO 00/34419, 2000.
108. Street, P. & Thorley, D. Solubilizing process. PCT WO 99/52996, 1999.
109. Mayerhofer, H., Schneider, W., Nüring, A. & Exner, W. Treibstoff sowie Zusatz zu dessen Herstellung. DE 2 216 880, 1971.
110. Lo, S. Y. A combustion enhancing fuel additive comprising microscopic water structures. PCT WO 97/18279, 1997.
111. Bertha, A. Additive for stabilizing water-containing fuels and a fuel stabilized with this additive. PCT WO 00/69999, 2000.
112. Wenzel, D. An additive composition also used as a fuel composition comprising water-soluble alcohols. PCT WO 99/35215, 1999.
113. Hazel, C. J. & Williamson, I. V. Fuel composition. PCT WO 00/36055, 2000.
114. Demirbas, A. Conversion of biomass for blending gasoline as an alternative fuel. *Energy Sources*, 2001, **23**(6), 553–562.
115. Marshall, E. D., Rodney, L. S. & Wheeler, C. C. (Texaco Inc.). Conversion of hazy gasoline to clear stable gasoline. US 4 568 345, 1986.
116. Hüffer, S., Mock-Knoblauch, C., Schürmann, G. & Lange, A. (BASF AG). Emulgatoren, insbesondere auf Basis von Polyisobutylenamine. DE 10109845, 2002.
117. Tanaka, Y. Petroleum fuel additive for power up and exhaust gas treatment. JP 2002060764, 2002. C.A. 136: 202884.
118. Hicks, R. H. & Song, B. C. Micro-emulsion fuel additive. US 2002095859, 2002.
119. Hart, P. R., Meyer, E. M. & Calvert, N. R. Stabilizer blends for alcohol in hydrocarbon fuel. PCT WO 02/059236, 2002.
120. Bongart, F., Hodgson, W., Rae, A. & Roeder, J. Alkoxylated esters and ethers as solubilizers for motor fuel-alcohol blends. PCT WO 02/038709, 2002.

Edusammud bensiini lisandite uurimisel

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On esitatud ülevaade bensiini lisandite kasutamisest, uurimistöö arengust ja viimase aja saavutustest. Käesoleval ajal pole võimalik tagada mootorite stabiilset funktsioneerimist ja mootori heitgaasides mürgiste komponentide kontsentratsiooni vähendamist, ilma et kasutataks bensiini lisandeid. Lisandeiks on vahendid, mis vähendavad mootori saastumist, parandavad detonatsioonikindlust ja põlemisprotsessi, stabiliseerivad bensiini, vältimaks oksüdatsiooni, polümerisatsiooni ja polükondensatsiooni ning ka mootori korrosiooni või mis muul moel aitavad säästa mootorit. Olulisimaiks lisandeiks on kujunenud detergendid, mis vähendavad mootori saastumist. Etanooli, vähese vee ja teiste lisanditega rikastatud bensiinisegu parandab põlemisprotsessi mootoris, see tagab kütuse kulu vähenemise ja puhtama õhu.