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UTJECAJ ADITIVACIJE MOTORNOG BENZINA NA UBRZANJE, SNAGU I EMISIJU ISPUŠNIH PLINOVA

Sažetak

Primjena aditiva u motornim benzinima stara je gotovo koliko i benzin sam. Rad se bavi kratkom poviješću aditivacije benzina, opisom učinaka pojedinih vrsti aditiva te mogućnostima njihova korištenja u motornim benzinima u sadašnjem trenutku kao i u bliskoj budućnosti.

1. Uvod

Proizvodnja motornih benzina bez primjene aditiva za različite svrhe praktično više nije zamisliva. Velika evolucija motoristike, trajan razvoj benzinskih motora, pojačani zahtjevi vezani uz zaštitu okoliša te sve snažnija konkurencija na tržištu motornih goriva postavljaju zahtjeve na kakvoću benzina, pri čemu aditivi imaju nezamjenjivu ulogu. Najveća prednost aditiva leži u činjenici što su već u vrlo malim dozama, počam od nekoliko stotina mg/kg, kadri izmijeniti svojstva benzina do one mjere do koje bi se to inače moglo postići jedino promjenom proizvodne tehnologije uz nerazmjerno velike troškove. U nekim slučajevima postizanje traženih svojstava benzina bez primjene aditiva a samo putem tehnoloških prilagodbi praktično čak nije niti moguće.

2. Kratka povijest

Aditivi za motorne benzine prvi se puta spominju u prvom desetljeću prošloga stoljeća. U to je vrijeme, naime, započela primjena spojeva na osnovi alkilnitrata, nitrofenola ili kamfora za poboljšanje izlazne snage motora.

U prvome i drugome desetljeću prošloga stoljeća izraženi su napori za poboljšanjem svojstava motornih benzina protiv lupanja, radi potrebe za povećanjem omjera stlačivanja a time i učinkovitosti i snage motora. Na temelju opsežnih istraživanja tvrtke General Motors Corporation započela je primjena tetraetil olova (TEO) kao

sredstva protiv lupanja: navedeni se spoj može smatrati prvim benzinskim aditivom proizvedenim na industrijskoj razini. Primjena TEO-a u više od 80 godina ostaje trajno povezana s imenima njegovih izumitelja Thomas Midgleya i T. A. Boyda. Aditivi koji konkuriraju tetraetil olovu razvijeni su praktično u isto vrijeme i nikada nisu postigli primjenu na komercijalnoj osnovi.

Uvođenje postupka termičkog krekiranja 1920-ih uvelo je potrebu za razvijanjem i primjenom jedne druge vrste aditiva, a to su antioksidanti, čije je korištenje potrebno za sprječavanje stvaranja smola u tako proizvedenim motornim benzinima. Praktično do današnjega dana kao antioksidanti se primjenjuju alkilfenoli, aminofenoli i alkil-supstituirani fenilendiamini.

Nakon Drugoga svjetskoga rata, uglavnom 1950-ih, započinje veliki razvoj aditiva za motorne benzine. Potreba zaštite od paljenja uzrokovana užarenim česticama nastalim uglavnom prekomjernom primjenom TEO u visoko oktanskim motornim te nadasve avio benzinima, potakla je korištenje alkilfosfatnih aditiva, čija je primjena, nakon određene izmjene sastava, započela kao primjena prvih detergentnih aditiva za usisne grane motora, a kasnije i za rasplinjač (npr. DMA 4 proizvođača DuPont). Otprilike u isto vrijeme dolazi do pojave antikorozijskih spojeva i inhibitora zaleđivanja za rasplinjač.

Nakon razmjerno mirna razdoblja 1960-ih, sedamdesete se odlikuju uvođenjem detergentnih sredstava za sve usisne grane, uključujući rasplinjače (detergentni aditivi druge generacije, npr. Chevronov F-310 ili Shellov ASD), primjereni ne samo za motore s rasplinjačem, već i za sustave ubrizgavanja goriva.

Prijelaz iz 1980-ih u devedesete obilježen je početkom proizvodnje bezolovnih benzina u Europi, aditiva za zaštitu sjedišta ispušnih ventila i najnovije generacije detergentnih aditiva odgovornih za minimalno stvaranje taloga u komori izgaranja.

Danas, na početku trećega tisućljeća, sa stajališta povijesti primjene aditiva, drugo je stoljeće njihova korištenja usmjereno poboljšanju kemijskog sastava detergentnih sredstava kao i razvoju novih tipova aditiva čija je primjena orijentirana prema korisnicima, uz predviđanje niže potrošnje goriva i ostalih željenih primjenskih svojstava (mazivost, ubrzanje).

3. Zahtjevi za kakvoćom motornih benzina

Pojedinačna svojstva motornih benzina mogu se podijeliti u dvije glavne skupine.

Prvu skupinu tvore svojstva što ih zahtijeva norma kakvoće - EN 228:2004. Razvoj ove norme i pojedinačnih parametara kakvoće može se smatrati posljedicom konsenzusa njihovih tvoraca, koji u pravilu podrazumijevaju sljedeće tri strane:

- ✓ proizvođači automobila,
- ✓ zaštitari okoliša,
- ✓ naftna industrija.

Zahtjevi navedenih strana glede svojstava motornih benzina prikazani su u tablici 1.

Tablica 1: Zahtjevi s obzirom na kakvoću motornog benzina

Proizvođači automobila	Zaštitari okoliša	Naftna industrija
IOB, MOB Destilacijska svojstva Tlak para Oksidacijska stabilnost Postojeći sadržaj smola Sadržaj Pb, P, S Prikladni aditivi Sadržaj oksigenata	Sadržaj olova Sadržaj sumpora Sadržaj benzena Sadržaj aromata Sadržaj olefina % isparljivosti V/V pri 150 °C(E150) Kraj destilacije Tlak para	Minimalne promjene u odnosu na prethodne norme

Druga skupina zahtjeva predstavlja složena svojstva svakako obilježena primjenskim svojstvima. Za njihovo su oblikovanje odgovorne sljedeće strane:

- ✓ proizvođači automobila (motora),
- ✓ zaštitari okoliša,
- ✓ kupci (vozači),
- ✓ konkurencija na tržištu goriva.

Za razliku od norme koja predstavlja konsenzus zainteresiranih strana, pri čemu se pojedinačni zahtjevi i njihove vrijednosti mogu smatrati minimalnima, strane odgovorne za formulaciju korisničkih svojstava nisu dužne u obzir uzeti zahtjeve i mogućnosti ostalih partnera. Radi toga su navedeni zahtjevi obično stroži. Zahtjevi uporabnih svojstava motornih benzina kao i oblici njihova zahtijevanja prikazuje t. 2.

Tablica 2: Utjecaj mogućih čimbenika na primjenska svojstva motornih benzina

Čimbenici			
Proizvođači automobila	**Zaštitari okoliša**	**Korisnici (vozači)**	**Konkurencija na tržištu**
Bez metala (Fe, Mn, ..) Bez silicija Čistoća rasplinjača Čistoća brizgaljki goriva Čistoća usisnog ventila Bez zaglavljivanja usisnog ventila Minimalni talozi u komori izgaranja	Emisije ispušnih plinova Emisije CO_2 Sadržaj komponenti iz obnovljivih izvora	Vozivost Potrošnja Snaga motora Ubrzanje vozila Radni vijek motora Vrijeme skladištenja motornog benzina	„Naš proizvod je najbolji na tržištu”
Oblici zahtijevanja / utvrđivanja svojstava			
Svjetska povelja o gorivima	Zakoni, akti Direktive o zaštiti okoliša	Predmet tržišnog zanimanja Ispitivanja motornih benzina u časopisima	Niveliranje Reklame konkurenata

4. Vrste aditiva motornih benzina

Spektar aditiva koji se primjenjuju u motornim benzinima uključuje sljedeće vrste:

- ✓ aditivi protiv lupanja,
- ✓ aditivi protiv zaleđivanja,
- ✓ antioksidanti,
- ✓ deaktivatori metala,
- ✓ inhibitori korozije,
- ✓ deemulgatori,
- ✓ aditivi protiv uleknuća sjedišta ventila,
- ✓ detergenti / Aditivi kontrole taloga,
- ✓ poboljšivači mazivosti,
- ✓ poboljšivači štednje goriva,
- ✓ ubrzivači.

Aditivi protiv lupanja (tetraetil olovo - TEO, tetrametil olovo - TMO, metilciklopentadien mangan trikarbonil - MMT) imaju u načelu dvije funkcije. Prva je povećanje oktanske razine benzina. Druga, a to je zaštita od uleknuća sjedišta ispušnog ventila, zapravo je jasnije primijećena tek prilikom postupnog ukidanja primjene ovih aditiva. Pojava uleknuća sjedišta ispušnog ventila poznata je u stvari još od početka prošloga stoljeća. Zahvaljujući činjenici što je taj problem riješen "sam od sebe" nakon uvođenja primjene TEO, nekoliko desetaka godina nije mu bila posvećivana više nikakva pozornost. Iako se primjena TEO u brojnim zemljama smatra prošlošću (u Slovačkoj je to slučaj već više od 10 godina), još uvijek ima zemalja u Europi u kojima proizvodnja i potrošnja olovnih benzina i dalje predstavlja stvarnost.

Aditivi protiv zaleđivanja mogu se spomenuti jedino s povijesnog stajališta, budući da su njihovu funkciju preuzeli detergentni aditivi. Ovi su izvorni aditivi bili primjenjivani 1950-ih i to podijeljeni u dvije skupine:

a. Depresanti krutišta koji su otapali nakupine leda na sapnici rasplinjača. U tu su svrhu korišteni metanol ili izopropilni alkohol u koncentraciji od 0,5 - 2 % V/V. Veća je učinkovitost postignuta korištenjem metilformamida, propilenglikola ili heksandiglikola u koncentraciji od 0,02 – 0,2 % V/V.
b. Površinski aktivne tvari koje su prianjanjem uz površinu rasplinjača onemogućavale stvaranje leda. U tu su svrhu korišteni amidi alkilfosfata, alkil-monoamini, alkil-diamini i imidazoli u koncentraciji od 0,002 do 0,01 % V/V. Navedene vrste aditiva nazivaju se detergentnim aditivima druge generacije.

Aditivi protiv uleknuća sjedišta ventila (AVSRA) – štite sjedišta ispušnih ventila od trošenja kod primjene bezolovnih benzina, uglavnom u vozilima koja nisu predviđena za korištenje čistih bezolovnih benzina. Obično sadrže organski vezane alkalijske metale (Na, K). U nekim su se zemljama (jugoistočna Azija) također koristili ili se još uvijek koriste i cinkovi alkilfosfati ili MMT. Aditivi ove vrste dodaju se u benzin u rafinerijama ili u otpravnim terminalima ili ih se pak može nabaviti u

maloprodaji na benzinskim crpkama. Pregled korištenja aditiva AVSRA, kao i oblik njihove primjene, dokumentirani su u tablici 3. Podaci u zagradama odnose se na godinu njihova uvođenja na tržište.

Antioksidanti sprječavaju kemijske reakcije što bi ih mogle izazvati različite kondenzirajuće visokomolekularne tvari uz moguće stvaranje smola (reakcije nezasićenih ugljikovodika koji postoje u gorivu s okolnim kisikom). Rezultat njihova djelovanja je zadržavanje performanci goriva kroz dugo vremensko razdoblje, što je vrlo povoljno kod skladištenja. Istodobno jamče također i smanjenje mogućnosti stvaranja taloga na stabljici ventila, što može uzrokovati zaglavljivanje ventila. Kao antioksidanti primjenjuju se alkilfenoli, aromatski amini i alkilno supstituirani aromatski amini.

Deaktivatori metala fiksiraju metale (prvenstveno Cu, Ag), koji putem katalitičnog učinka ubrzavaju procese oksidacije u motornom benzinu. U tu se svrhu koriste spojevi koji mogu fiksirati metale u stabilnim kelatnim spojevima.

Inhibitori korozije polarnim stranama molekula prekrivaju metalnu površinu i tako sprječavaju njezin doticaj s tvarima (voda, zrak), koje bi mogle izazvati koroziju. Izvori vlage u motornom benzinu su neki tehnološki procesi ili disanje spremnika. Kao inhibitori korozije, koriste se organske kiseline i njihovi derivati. Neke vrste inhibitora mogu imati također i maziva svojstva.

Tablica 3: Početak primjene i oblici aditiva protiv uleknuća sjedišta ventila (AVSRA)

AVSRA dodani u rafinerijama (zajednički aditivni tretman)	AVSRA dodani od strane korisnika (poslijeprodajni aditivni tretman)
Austrija - SuperPlus 98 (1990. – 1999.)	Austrija (1990.)
Slovačka - Regular 91 (1992.)	Slovačka (1990.)
Švedska (1992.)	Češka Republika (1993.)
Norveška (1992.)	Belgija
Slovačka - Super 95 (1993. – 2001.)	Estonija
Finska (1993.)	Njemačka
Danska (1993. – 1994.)	Mađarska
Nizozemska (1996.)	Italija
Mađarska - SuperPlus 98 (1999.)	Latvija
Portugal (1999.)	Litva
Velika Britanija - Super 97 (1999.)	Poljska
Francuska (2000.)	Portugal
Španjolska (2001.)	Španjolska
Češka Republika - Regular 91 (2002.)	Švicarska
Grčka (2002.)	
Bugarska - Regular 91 (2002.)	

Deemulgatori poboljšavaju (ubrzavaju) odjeljivanje vode od motornog benzina, osobito u slučajevima kada je to prirodno svojstvo ugljikovodičnog goriva ograničeno doziranjem površinski aktivnih aditiva (inhibitora korozije, AVSRA, detergentnih

aditiva). Učinak deemulgatora primijenjenih u motornom benzinu posebno je važan zimi, jer je putem njihove primjene moguće spriječiti stvaranje leda u cijevima za gorivo, što utječe na pokretanje motora.

Detergenti /Aditivi kontrole taloga zasad pripadaju među najvažnije aditive koji se primjenjuju u bezolovnim motornim benzinima. Detergenti čiste i održavaju čistoću čitavog sustava za gorivo - spremnika, rasplinjača ili sustava ubrizgavanja, usisnih grana, usisnih ventila, te istodobno smanjuju talog u komori za izgaranje. Kada u motornome benzinu ne bi bilo detergenata, nakupljanje bi taloga otežalo stvaranje smjese zraka i goriva čime bi se ujedno pogoršala i svojstva ispušne emisije i povećala potrošnja goriva. Veća količina taloga u komori izgaranja povećava oktanski zahtjev motora.

Primjena detergenata u motornim benzinima potječe iz 1950-ih, ali je prva generacija detergenata na osnovi amino-amida i alkil sukcinimida pokazala tek ograničenu učinkovitost, a u slučaju rasplinjača i brizgaljki ujedno i paralelni negativan učinak stvaranja taloga na ulaznim ventilima i usisnoj grani (osobito u doziranju od preko 80 ppm). Stoga je na prijelazu iz 1960-ih u 1970. započela primjena detergenata druge generacije. Ti su detergenti bili na osnovi polibuten sukcinimida. Treća generacija detergenata - poliizobutenamini (PIBA) uvedena je sredinom 1980-ih te su aditivi te generacije pokazali pozitivan učinak čišćenja prethodno nakupljenih taloga na usisnim ventilima. Od samoga početka druge generacije, detergenti, osim amida i amina, sadrže također i tzv. tekućine nositelje aditiva. Isprva su u tu svrhu korištena bazna ulja naftenske osnove (SAE 30), kasnije sintetička ulja, a počam od treće generacije sintetički polieteri. Primjena polietera rezultirala je smanjenjem taloga u komori izgaranja, osobito u usporedbi s drugom generacijom i kombinacijom PIBA + ulje.

Četvrtom se generacijom detergenata smatraju aditivi na osnovi polieter amina (PEA). Razvijeni su posebno za bezolovne benzine te njihova uporaba ne zahtijeva nikakvu tekućinu kao nositelj. Aditivi PEA koriste se također i u kombinaciji s PIBA kada se zahtijeva viša razina detergencije. Obje vrste polimernih aditiva aminskog tipa dokazale su sposobnost sprječavanja odnosno minimizacije stvaranja taloga u motorima suvremenih vozila, uključujući ne samo usisne grane, usisne ventile i sustave ubrizgavanja, već i komore izgaranja.

Iako detergentna svojstva motornih benzina nisu propisana normama kakvoće (STN EN 228), već se više od 20 godina aditivi te vrste primjenjuju u većini europskih zemalja. U bivšoj je Čehoslovačkoj primjena detergenata započela 1984. U češkim se rafinerijama upotrebljava aditiv SAP 941, a u Slovnaftu aditiv SAP 942, koji su oba proizvodi tvrtke Shell.

Trajno poboljšanje učinkovitosti detergentnih aditiva ne samo za usisni sustav već i za komore izgaranja često se koristi u reklamne svrhe, za pribavljanje kupaca na tržištu motornih benzina. Dosad opisane aditive, uz iznimku onih povijesnih (TEO, TMO, MMT, aditivi protiv zaleđivanja), možemo smatrati suvremenima, te se njihovo korištenje predviđa također i za bližu budućnost. Zadnje tri vrste aditiva: aditivi za

poboljšanje mazivosti, štednju goriva i ubrzanje, nalaze se praktično u razvojnoj fazi, jednako u smislu kemijskoga sastava kao i primjene na tržištu.

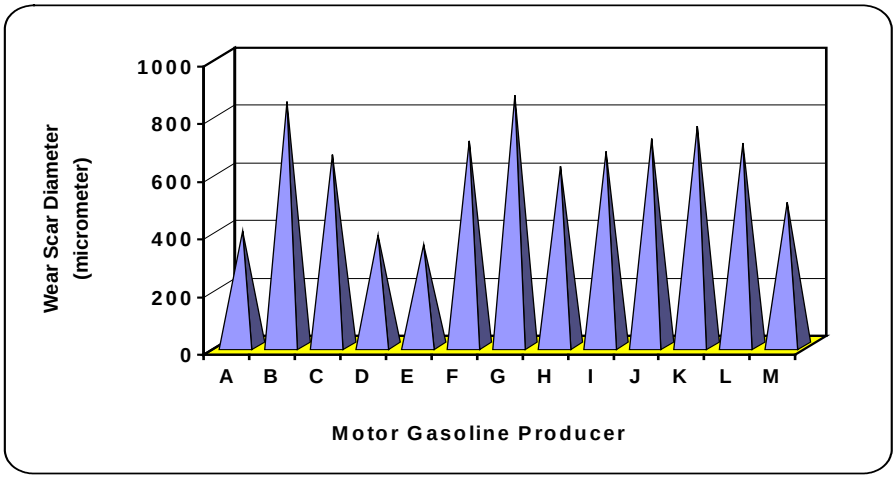
Kao motiv primjene **aditiva mazivosti** možemo smatrati daljnje postroženje zahtjeva za kakvoćom motornih benzina sadržanih u ažuriranome standardu EN 228:2004, kojim se, počam od 1. siječnja 2005, zahtijeva smanjenje količine aromata na granicu od maks. 35 % V/V te uvode motorni benzini sa sadržajem sumpora od maks. 10 mg/kg. Navedeni čimbenici, zajedno s rastućom populacijom vozila s tehnologijom izravnog paljenja benzina (tlak u crpki za ubrizgavanje danas dosiže i do 10 MPa), može pokrenuti pravu "lavinu" primjene aditiva mazivosti u motornim benzinima. Prve je naznake moguće već zamijetiti, što se može potkrijepiti vrijednostima svojstava mazivosti motornog benzina Super RON 95, dostupnoga na tržištu srednje Europe. Usporedbom prikazanih podataka s mazivošću glavnih sastojaka motornog benzina možemo zaključiti kako motorni benzini nekolicine tvrtki već sadrže aditiv mazivosti, iako sve one službeno to još ne ističu.

Primjena **aditiva za štednju goriva** i **poboljšanje ubrzanja** mogla bi u budućnosti postati sredstvom privlačenja većeg broja vozača na benzinske crpke onih tvrtki koje će svojim kupcima biti u mogućnosti ponuditi takav aditiv. S obzirom na razmjerno visoku cijenu navedenih aditiva, kao i veliku količinu potrebnu za postizanje željenog učinka, još je uvijek upitno hoće li se ti aditivi izravno dodavati u motorne benzine ili će se pak vozačima nuditi u maloprodaji. Za dokaz da je riječ o visoko sofisticiranim proizvodima, upućujemo čitatelje na rezultate učinkovitosti dobivene putem ispitivanja na motorima.

Tablica 4: Učinak vrste aditiva na potrošnju goriva pri trajnim brzinama i ispitivanju ECE 83

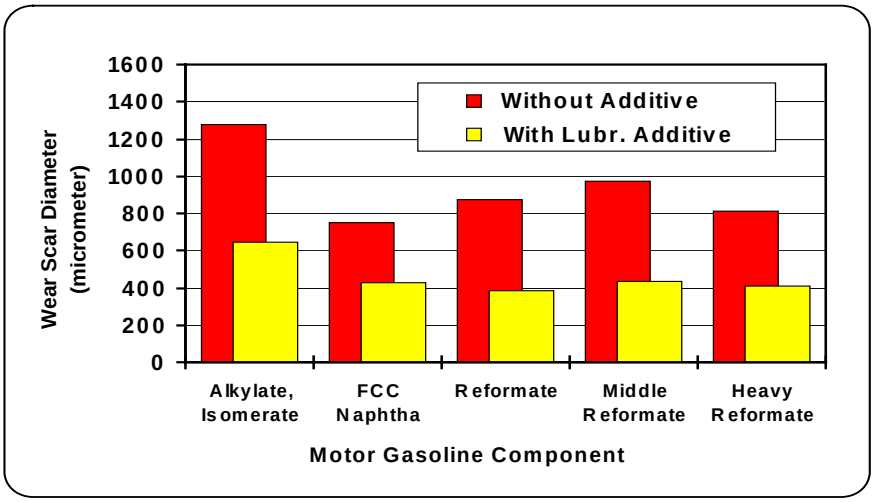
Doziranje aditiva	Vrsta aditiva	Poboljšanje (%)			
		60 km/h	90 km/h	120 km/h	Ispitivanje ECE 83
	Aditiv - A (VURUP)	0,3	0,7	0,2	1,7
	Ubrzivač	1,3	0,3	0,8	0,8
	Aditiv - B (VURUP)	3,2	2,0	1,7	2,3
Nisko	Aditiv za štednju goriva	1,7	0,6	1,3	1,2
	Aditiv - A (VURUP)	0,3	1,7	0,6	0,2
	Ubrzivač	1,6	0,7	1,9	0,9
	Aditiv - B (VURUP)	3,2	2,3	2,1	1,7
Srednje	Aditiv za štednju goriva	3,3	2,2	2,1	1,7
	Aditiv - A (VURUP)	3,7	2,9	1,2	3,1
	Ubrzivač	1,7	0,4	0,3	1,5
	Aditiv- B (VURUP)	3,6	1,9	1,9	2,9
Visoko	Aditiv za štednju goriva	3,7	2,5	2,5	2,8

Slika 1 Mazivost motornog benzina Super RON 95 na benzinskim crpkama odabranih tvrtki srednje Europe
Figure 1 Lubricity of motor gasoline Super RON 95 at the filling stations of selected companies in Central Europe



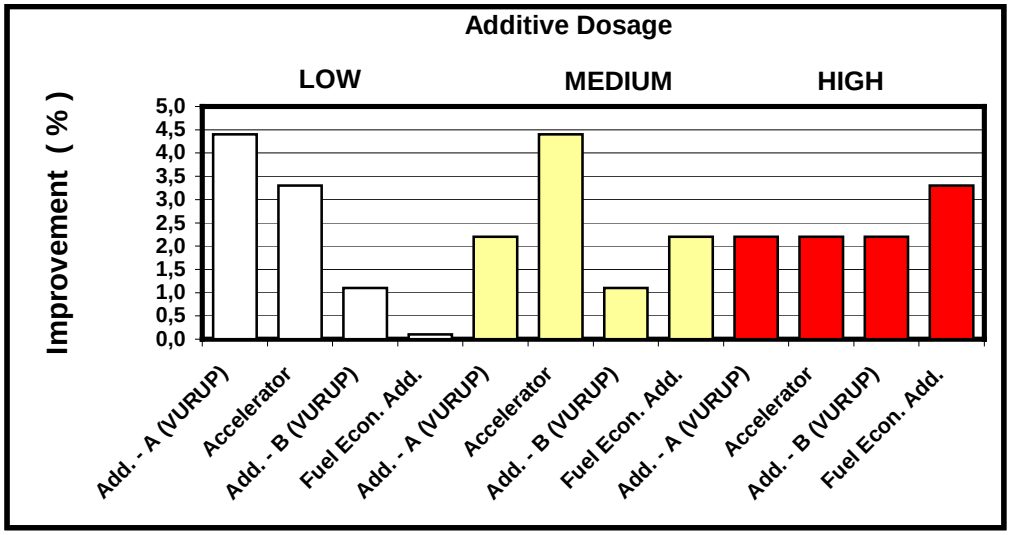
Promjer traga trošenja / Proizvođač motornog benzina/

Slika 2: Mazivost glavnih sastojaka motornog benzina
Figure 2: Lubricity of motor gasoline main components



Promjer traga trošenja Bez aditiva / S aditivom za mazivost
Alkilat, izomerat FCC benzin Reformat Srednji reformat Teški reformat Sastojak m. benzina

Slika 3: Učinak vrste aditiva na poboljšanje snage motora
Figure 3: Effect of additive type on engine power improvement



Poboljšanje Doziranje aditiva
NISKO SREDNJE VISOKO
Ad. A Ubrzivač Ad. B Aditiv za štednju goriva

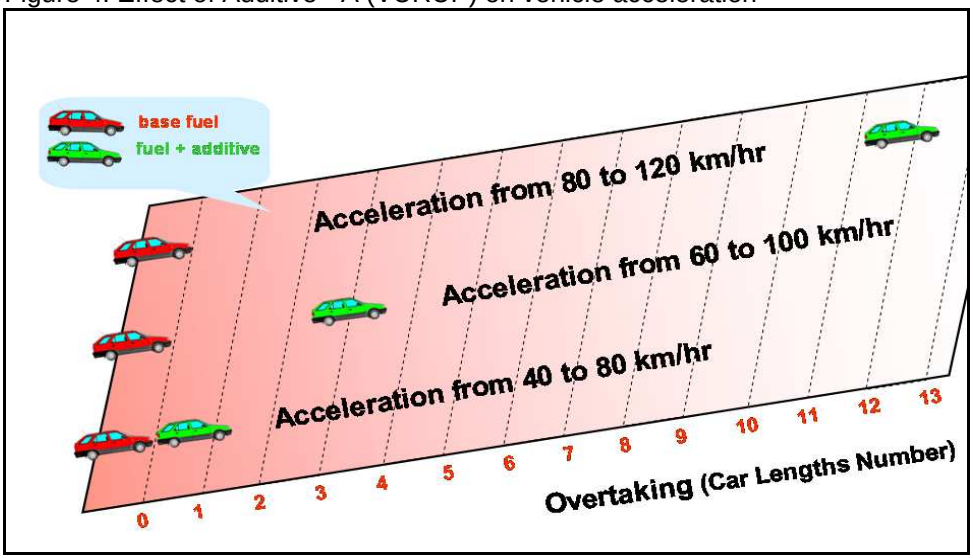
Tablica 5: Učinak vrste aditiva na emisiju ugljikovodika pri trajnim brzinama

Doziranje aditiva	Vrsta aditiva	Poboljšanje (%)		
		60 km/h	90 km/h	120 km/h
	Aditive - A (VURUP)	23,0	16,1	14,7
	Ubrzivač	22,2	28,4	10,7
	Aditiv - B (VURUP)	33,2	27,9	21,8
Nisko	Aditiv za štednju goriva	24,6	16,5	14,2
	Aditiv - A (VURUP)	31,7	29,9	18,3
	Ubrzivač	29,1	22,8	16,0
	Aditiv - B (VURUP)	34,0	28,4	21,8
Srednje	Aditiv za štednju goriva	24,8	27,0	21,8
	Aditiv - A (VURUP)	36,4	26,0	2,8
	Ubrzivač	29,3	17,9	14,2
	Aditiv - B (VURUP)	29,3	22,8	18,3
Visoko	Aditiv za štednju goriva	35,0	23,2	17,1

Tablica 6: Učinak vrste aditiva na emisiju dušikovih oksida pri trajnim brzinama

Doziranje aditiva	Vrsta aditiva	Poboljšanje (%)		
		60 km/h	90 km/h	120 km/h
Nisko	Aditiv - A (VURUP)	18,6	3,8	5,7
	Ubrzivač	7,0	11,8	4,0
	Aditiv - B (VURUP)	16,0	4,7	8,3
	Aditiv za štednju goriva	18,3	11,6	6,7
Srednje	Aditiv - A (VURUP)	22,4	11,8	5,3
	Ubrzivač	20,0	8,8	0,4
	Aditiv - B (VURUP)	27,7	5,8	0,1
	Aditiv za štednju goriva	26,8	11,9	1,5
Visoko	Aditiv - A (VURUP)	25,2	3,6	2,8
	Ubrzivač	24,3	2,0	0,9
	Aditiv - B (VURUP)	16,0	1,5	2,8
	Aditiv za štednju goriva	15,2	1,2	3,6

Slika 4: Učinak aditiva - A (VURUP) na ubrzanje vozila
Figure 4: Effect of Additive - A (VURUP) on vehicle acceleration



osnovno gorivo gorivo + aditiv
ubrzanje
pretjecanje (broj dužina vozila)

5. Zaključak

Različite su vrste aditiva postale sastavnim dijelom suvremenih motornih benzina te je danas gotovo nemoguće bez njih zamisliti proizvodnju benzina. Što se tiče njihovih učinaka, oni pomažu pri udovoljavanju zahtjevima kakvoće standarda EN 228, ispunjenju očekivanja proizvođača motora (vozila) navedenih u Svjetskoj povelji o gorivima, kao i očekivanja vozača. U nekim je slučajevima njihov doprinos također i ekološki.

Njihovu su razvoju složenim ispitivanjima i odabiru najpovoljnijih tipova i vrsta uložena golema novčana sredstva, stoga ne čudi kako se prednosti što ih nude opsežno objavljuju kako bi se na tržištu motornih goriva stekle određene komparativne prednosti.

IMPACT OF MOTOR GASOLINE ADDITIVE TREATMENT ON ACCELERATION, POWER OUTPUT AND EXHAUST EMISSION CHARACTERISTICS

Abstract

The additive application in motor gasolines has almost such long history as the motor gasolines themselves. The paper deals with a brief history of motor gasoline additive application, description of the effects of the individual additive sorts and possibilities of their usage in motor gasolines at present and in the near future respectively.

1. Introduction

The gasoline production at present is without the additive application of various stipulation practically not conceivable. Big evolution of motorism, incessant development of spark ignition combustion engine design, increase of requirements as for the environmental protection and still stronger competition on the motor fuel market create demands on the motor gasoline quality at fulfilment of them the additives play their non-substituted role. The biggest advantage of additives is that in

very small dosages since some hundreds of mg/kg they are able to modify the gasoline properties in such extend which would be realistic only at alteration in production technology at abnormal high expenses. In some cases the required properties of gasolines without the additive application are through the technological adjustment even practically not available.

2. Short history

The first references as for the motor gasoline additives are dated from the first decade of past century. For power output improvement of the engines at that time the compounds of the alkylnitrates, nitrophenols type or camphor begun to be applied.

In 1910´s and 1920´s the effort for improvement of anti-knocking properties of motor gasolines is evident owing a need for increase of compression ratio and therefore the engine efficiency and power characteristics. As a result of extensive research in General Motor Corporation the application of tetraethyl lead (TEL) as an anti-knocking agent is known and therefore the above compound can be considered for the first gasoline additive produced in an industrial scale. The application of TEL during more than 80 year period remains for ever connected with the names of its inventors namely Thomas Midgley and T. A. Boyd. To tetraethyl lead “competitive” additives which were developed practically in the same time period has never found the application on a commercial basses.

The introducing of the thermal cracking process in 1920´s has demanded the development and the application of another type of additives - namely anti-oxidants, usage of which was necessary for the prevention of the gum formation in such produced motor gasolines. Practically to this day as anti-oxidants are applied alkylphenols, aminophenols and alkyl-substituted phenylenediamines.

After World War II, mainly in 1950´s the big development of motor gasoline additives has been started. The need for protection against the ignition initiated by glow points, which were created predominately by excessive application of TEL in high octane motor and above all in aviation gasolines incurred the usage of alkylphosphate additives, which after some alteration of their composition begun to be applied as the first detergent additives for engine intake manifolds and afterwards also for carburettor (e.g. DMA 4 produced by DuPont). In the same time period also the appearance of anti-corrosion compounds and ice inhibitors for carburettors are dated.

After the relatively smoothly time period of 1960´s the 1970´s are characterised by introduction of the detergent agents for all the intake systems including carburettors (detergent additives of the second generation, e.g. F-310 produced by Chevron or ASD by Shell), which were suitable not only for the engines with carburettors but also for fuel injection systems.

At the tern of 1980´s and 1990´s characterised by the start of unleaded gasolines production in Europe the additives for protection of the exhaust valve seats and

latest generation of detergent additives responsible for minimum combustion chamber deposits has been developed.

At present namely at the beginning of the third millennium and from the viewpoint of the additive application history their second century usage the development is oriented on the improvement of the chemical structure of detergent agents as well as the evolution of the new additive types with the customer's oriented application - with prediction of lower fuel consumption and other utility properties (lubricity, acceleration).

3. Requirements for Motor Gasoline Quality

The individual motor gasoline properties can be divided into two principal groups.

The first group is represented by the properties required by the qualitative standard - EN 228:2004. The genesis of the standard and values of the individual qualitative parameters can be considered for a consensus of its authors who as a rule represent the following three parties:

- ✓ Automobile manufacturers,
- ✓ Environment representatives,
- ✓ Oil industry.

Requirements of the above parties as for the motor gasoline properties are presented in table 1.

Table 1: Requirements of standard authors on the motor gasoline quality

Automobile manufacturers	Environment representatives	Oil industry
RON, MON Distillation properties Vapour pressure Oxidation stability Existent gum content Content of Pb, P, S „Suitable" additives Oxygenates content	Lead content Sulphur content Benzene content Aromatics content Olefins content Evaporated % V/V at 150 °C (E150) Final boiling point Vapour pressure	Minimal changes towards previous standard issue

The second group of the requirements represents the complex of properties which are obviously marked as the utility properties. For their formulation the parties as follows are responsible:

- ✓ Automobile (engine) manufacturers,
- ✓ Environment representatives,
- ✓ Customers (motorists),

- ✓ Competition on fuel market.

As distinct from the standard which is created as a consensus of participating parties and so the individual requirements and their values can be considered as minimal ones, the parties responsible for the utility properties formulation are not obliged to mind the requirements and possibilities of the other partners. From this reason the requirements are usually more severe. The requirements as for the motor gasoline utility properties as well as the forms of their claiming are presented in table 2.

Table 2: Effect of the possible factors on motor gasoline utility properties

Factors **Automobile manufacturers**	**Environment representatives**	**Customers (motorists)**	**Competition on market**
No metals (Fe, Mn, ..) No silicone Carburettor cleanliness Fuel injector cleanliness Intake valve cleanliness No intake valve sticking Minimal combustion chamber deposits	Exhaust emissions CO_2 emissions Content of components from renewable sources	Driveability MoGas consumption Engine power Vehicle acceleration Engine service life MoGas storage life	„Our MoGas is the best one on the market"
Forms of requiring / determination of utility properties			
World-Wide Fuel Charter	Laws, Acts Environmental Directives	Object of market interest Motor gasoline tests in journals	Benchmarking Advertisement of competitors

4. Sorts of Motor Gasoline Additives

The spectrum of additives applied in motor gasolines includes the types as follows:

- ✓ Antiknock additives,
- ✓ Anti-icers,
- ✓ Antioxidants,
- ✓ Metal deactivators,
- ✓ Corrosion inhibitors,
- ✓ Demulsification agents,
- ✓ Anti valve seat recession additives,
- ✓ Detergents / Deposit control additives,
- ✓ Lubricity improvers,
- ✓ Fuel economy improvers,
- ✓ Accelerators.

Antiknock additives (tetraethyl lead - TEL, tetramethyl lead - TML, methylcyclopentadiene manganese tricarbonyl - MMT) have in principle two functions. The first

one is the increase of gasoline octane levels. The second one namely the protection against the exhaust valve seat wear (recession) has been "discovered" only during the phase-out of the application of these additives. The discovery of the function number two is cited in quotation marks therefore that the phenomenon of the exhaust valve seat wear is known since the beginning of the last century. Due to the fact that this problem was solved "by itself" after the introduction of TEL application no adequate intentness has been dedicated to it for several tens of years. Although the TEL application in many countries is considered to be a history (in Slovakia more than 10 years) after all in some European countries the production and distribution of leaded gasolines is still the reality.

Anti-icers can be quoted only from the historical viewpoint thereof their function has been taken over by detergent additives. Original additives have been applied in 1950´s and were divided into two groups:

a. Depresants of freezing point which melted the ice formations on the carburettor nozzle. For this purpose methanol or isopropyl alcohol in the concentration of 0.5 - 2 % V/V has been applied. Higher efficiency was arrived at the usage of methylformamide, propyleneglycol or hexanediglycol applied in the concentration of 0.02 – 0.2 % V/V.
b. Surface-active substances which through the adhesion on the surface of carburettor parts disabled the ice creation. For this purpose amides of alkylphosphate, alkyl-monoamines, alkyl-diamines and imidazoles in the concentration from 0.002 too 0.01 % V/V were applied. These types of additives are obviously named as the detergent additive of the second generation.

Anti Valve Seat Recession Additives (AVSRA) - protect seats of exhaust valves against the wear at the application of unleaded gasolines predominantly at the cars which are not designed for application of pure unleaded gasolines. Usually they content organic bounded alkaline metals (Na, K). In some countries (Southeast Asia) also zinc alkylphosphates or MMT were/are used. Additives of this type are added to the gasolines either in refineries and/or at expedition terminals or they are available in the retail packing at the filling stations. The survey of AVSRA additive usage and the form of their application is documented in the table 3. The data in brackets stand for the year of their market introduction.

Antioxidants repress the chemical reactions which could create various condensing high-molecular substances with the possible inception of gums (reactions of in the motor fuel existing unsaturated hydrocarbons with the ambient oxygen). The result of their activities is maintenance the fuel performances for a long time period preferable at the storing. At the same time they guarantee also the decreasing of the probability of deposits creation at the valve stems which can cause the valve sticking. As antioxidants alkylphenols, aromatic amines and alkyl substituted aromatic amines are applied.

Metal deactivators fix metals (preferably Cu, Ag), which can by catalytic effect accelerate oxidation processes in motor gasoline. For this purpose the compounds which are able to fix the metals in the stable chelate compounds are used.

Corrosion inhibitors with the polar parts of molecules they cover the metallic surface and thereof prevent the contact between it and those substances (water, air), which can cause the corrosion. The sources of humidity contained in motor gasoline are some technological processes or "breathing" of the tanks. As the corrosion inhibitors organic acids and their derivatives are used. Some kinds of inhibitors can have also lubricating properties.

Table 3: Start of application and forms of anti valve seat recession additives (AVSRA)

AVSRA added in refineries (bulk additive treatment)	AVSRA added by customers (additive aftermarket treatment)
Austria - SuperPlus 98 (1990 - 1999)	Austria (1990)
Slovakia - Regular 91 (1992)	Slovakia (1990)
Sweden (1992)	Czech Republic (1993)
Norway (1992)	Belgium
Slovakia - Super 95 (1993 - 2001)	Estonia
Finland (1993)	Germany
Denmark (1993 - 1994)	Hungary
Netherlands (1996)	Italy
Hungary - SuperPlus 98 (1999)	Latvia
Portugal (1999)	Lithuania
Great Britain - Super 97 (1999)	Poland
France (2000)	Portugal
Spain (2001)	Spain
Czech Republic - Regular 91 (2002)	Switzerland
Greece (2002)	
Bulgaria - Regular 91 (2002)	

Demulsification agents improve (accelerate) water separation from the motor gasoline especially in those cases when this natural property of hydrocarbon fuel is limited by the dosage of surface-active additives (corrosion inhibitors, AVSRA, detergent additives). The effect of demusification agents applied in motor gasoline is particularly important during the winter season, because through this application it is possible to prevent the creation of ice plugs in fuel pipes, which can render the engine starting.

Detergents / Deposit control additives belong at present among the most important additives which are applied in the unleaded motor gasolines. Detergents clean or keep clean the whole fuel system - fuel tank, carburettor or injection system, intake manifold, intake valves and at the same time decrease the deposit amount in combustion chambers. In the case that there will be no detergent in motor gasoline the creating deposits would deteriorate the conditions for formation of air-fuel mixture with the subsequent deterioration of exhaust emission characteristics and increased fuel consumption. The higher amount of deposits in combustion chambers increases the engine octane requirement.

The application of detergents in motor gasolines is dated from 1950´s but the first detergent generation on the basis of amine-amides and alkyl succinimides has shown only limited efficiency as for the carburettors and injectors at the parallel negative effect as for the creation of deposits on intake valves and intake manifolds (especially at the dosage over 80 ppm). Therefore at the turn of 1960´s and 1970´s the application of detergents of the second generation started. These detergents were on the basis of polybutene succinimides. The third detergent generation - polyisobutenamines (PIBA) has been introduced in the middle of 1980´s and the additives of this generation have shown the positive effect as for the cleaning of prior accumulated deposits on the intake valves. From the very beginning of the second generation, detergents apart from amide and amine components respectively contained also so called “caring fluids”. At the beginning the base petroleum origin oils (SAE 30) have been applied for this purpose, afterwards synthetic oils and from the third generation synthetic polyethers were/are used as caring fluids. The application of polyethers resulted in the reduction of the combustion chamber deposits especially comparing it with the second generation and the PIBA + oil combination respectively.

As the fourth detergent generation the additives on the basis of polyether amines (PEA) are declared. These were developed specially for the unleaded gasolines and their application does not require any caring oil. PEA additives are also used in the combination with PIBA when the higher level of detergency is required. Both sorts of polymeric additives of amine type have proved the ability to prevent respectively to minimize the deposit creation in the engines of modern cars including not only intake manifolds, intake valves injection systems but also the combustion chambers.

Although the detergent properties of motor gasolines are not prescribed by qualitative standards (STN EN 228), really for more than 20 years the additives of such a type have been applying in majority of European countries. In former Czechoslovakia the application of detergents started in 1984. In Czech refineries additive SAP 941 has been applied whereas in Slovnaft it was additive SAP 942, both products of Shell company.

Continual improvement of detergent control additives efficiency not only as for the intake system but also on combustion chambers is frequently used at propaganda and therefore at gaining of customers on the market with motor gasolines. Till now described additives, with the exception of historical ones (TEO, TMO, MMT, anti-icers), can be declared for contemporary ones and with the expectation of application also in the next future. Latest three additive sorts namely lubricity additives, fuel economy additives and acceleration improvers are practically in the development stage as for their chemical structure and implementation on the market.

As the motive for **lubricity additive** application can be considered the further severity of motor gasoline qualitative requirements represented by updated standard EN 228:2004, which will since January 1st, 2005 require decreasing of aromatics to the limit of max. 35 % V/V and introducing of motor gasolines with sulphur content

max. 10 mg/kg. These factors together with the increasing population of the cars with gasoline direct ignition technology (pressure in injection pump reaches nowadays as high as 10 MPa), can provoke “an avalanche” of lubricity additive application in motor gasolines. The first indications can be observed just at present what can be documented by the values of lubricity properties of motor gasoline Super RON 95 available on the Central European market. At the comparison of the presented data with the lubricity of motor gasoline main components can be concluded that the motor gasolines of several companies already contain the lubricity additive, although only a few of them declare this fact officially.

The application of **fuel economy additives** and **acceleration improvers** could in the next future become the tool to attract the higher number of motorists for filling stations of those companies which will be able to offer such a type of additive to their customers. Regarding to the relatively high prices of these additives and their high dosage needed for the required effect it is questionable if these additives will be added to the motor gasolines or they will be for disposal to the motorist in the retail packing. About the fact that these additives are not only ”monkey’s drops”, but they represent highly sophisticated products it is possible to learn from the efficiency results obtained by engine tests.

Table 4: Effect of additive type on fuel consumption at constant speeds and ECE 83

Additive Dosage	Additive Type	Improvement (%)			
		60 km/hr	90 km/hr	120 km/hr	ECE 83 test
	Additive - A (VURUP)	0,3	0,7	0,2	1,7
	Accelerator	1,3	0,3	0,8	0,8
	Additive - B (VURUP)	3,2	2,0	1,7	2,3
Low	Fuel Economy Additive	1,7	0,6	1,3	1,2
	Additive - A (VURUP)	0,3	1,7	0,6	0,2
	Accelerator	1,6	0,7	1,9	0,9
	Additive - B (VURUP)	3,2	2,3	2,1	1,7
Medium	Fuel Economy Additive	3,3	2,2	2,1	1,7
	Additive - A (VURUP)	3,7	2,9	1,2	3,1
	Accelerator	1,7	0,4	0,3	1,5
	Additive - B (VURUP)	3,6	1,9	1,9	2,9
High	Fuel Economy Additive	3,7	2,5	2,5	2,8

Table 5: Effect of additive type on hydrocarbon emissions at constant speeds

Additive Dosage	Additive Type	Improvement (%)		
		60 km/hr	90 km/hr	120 km/hr
	Additive - A (VURUP)	23,0	16,1	14,7
	Accelerator	22,2	28,4	10,7
	Additive - B (VURUP)	33,2	27,9	21,8
Low	Fuel Economy Additive	24,6	16,5	14,2
	Additive - A (VURUP)	31,7	29,9	18,3
	Accelerator	29,1	22,8	16,0
	Additive - B (VURUP)	34,0	28,4	21,8
Medium	Fuel Economy Additive	24,8	27,0	21,8
	Additive - A (VURUP)	36,4	26,0	2,8
	Accelerator	29,3	17,9	14,2
	Additive - B (VURUP)	29,3	22,8	18,3
High	Fuel Economy Additive	35,0	23,2	17,1

Table 6: Effect of additive type on nitrogen oxides emissions at constant speeds

Additive Dosage	Additive Type	Improvement (%)		
		60 km/hr	90 km/hr	120 km/hr
	Additive - A (VURUP)	18,6	3,8	5,7
	Accelerator	7,0	11,8	4,0
	Additive - B (VURUP)	16,0	4,7	8,3
Low	Fuel Economy Additive	18,3	11,6	6,7
	Additive - A (VURUP)	22,4	11,8	5,3
	Accelerator	20,0	8,8	0,4
	Additive - B (VURUP)	27,7	5,8	0,1
Medium	Fuel Economy Additive	26,8	11,9	1,5
	Additive - A (VURUP)	25,2	3,6	2,8
	Accelerator	24,3	2,0	0,9
	Additive - B (VURUP)	16,0	1,5	2,8
High	Fuel Economy Additive	15,2	1,2	3,6

5. Conclusion

The various sorts of additives became a part of modern motor gasolines and nowadays it is practically not thinkable to imagine the gasoline production without them. From the viewpoint of their effects they help to ensure qualitative requirements of the standard EN 228, then to fulfil the expectations of engine (car)

producers presented in World-Wide Fuel Charter, as well as the anticipations of motorists. In several cases they contribute toward the environmental improvements.

For their further development, complex tests and the selection of the most convenient types and sorts the huge financial accounts are invested and so it can be not surprised that their advantages are often widely published with the aim to gain the comparative benefits on the motor fuel market.

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665.733.5.035	primjenska svojstva motornog benzina	motor gasoline application properties
665.733.5.038	motorni benzin, aditivi i poboljšavanje svojstava	motor gasoline, additives and property improving
"1910-2005"	razdoblje 1910-2005.g.	time interval 1910-2005.y.
351.777 (4)	EU program za čišće motorno gorivo 1990-2009	EU programme for clean motor fuel 1990-2009 y.

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