

Chapter 2

Fuel Additives

All good things come in small packages.

The Russian proverb.

Abstract Most fuels such as gasoline, kerosene (jet fuel), gas oil (diesel fuel) and fuel oil have drawbacks which do not allow their long term storage, make difficult transportation and even use. About 20 properties of fuels can be improved, maintained or imparted new beneficial characteristics by the adding of small amounts of certain chemicals named *fuel additives*. Fuel additives are added in very small concentrations: from several ppm to several thousands ppm. It is important that additives which improve some properties should not deteriorate other properties of fuels and its quality in general. Fuel additives are organic substances soluble in fuels: antifoams, anti-icing additives, anti-knock additives, antioxidants, antistatic additives, anti-valve seat recession additives, biocides, cetane improvers, combustion chamber deposit modifiers, corrosion inhibitors, demulsifiers, deposit control additives, detergents, diesel fuel stabilizers, drag reducing agents, dyes and markers, leak detector additives, lubricity improvers, metal deactivators, and wax anti-settling additives. Additives to fuel oil also are described: demulsifiers, sludge dispersants, combustion improvers, and additives for prevention oil-ash and cold-end corrosion in boilers. Action of fuel additives, their application, risks and benefits are analysed.

Most fuels such as gasoline, kerosene (jet fuel), gas oil (diesel fuel) and fuel oil have drawbacks which do not allow their long term storage, make difficult transportation and even use. For example, certain components of fuels can be oxidized and their properties can be deteriorated. In this case, antioxidants, stabilizers and metal deactivators are injected into fuels. Jet fuel can be frozen at low ($< -49^{\circ}\text{C}$) temperatures. In this case, wax anti-settling additives diminishing freezing temperature of jet fuel are needed. If dissolved water is present in jet fuel, water can be turned into ice at $T < 0^{\circ}\text{C}$, which can clog filters, and fuel will not flow into engine. Such situation can cause crashes of airplanes. Anti-icing additives are needed in such cases. Sometimes contact of gasoline and kerosene (containing corrosive substances water and oxygen) with metallic equipment may result in corrosion. In this case, corrosion inhibitors are required for injection into fuels. If water appears in jet fuel or gas oil, microorganisms can proliferate and result in biofouling, deterioration of fuel properties, clogging of filters, screens, sump drains, valves, pipes where fuel flows into engines, their malfunctioning and uncontrolled severe corrosion. In this case,

biocides are needed to be injected into fuels. Complex hardware in modern engines led to the need for additives in the gasoline to keep carburetors, intake valves, injectors, sensors, and the pollution control devices clean and working well.

About 20 properties of fuels can be improved, maintained or imparted new beneficial characteristics by the adding of small amounts of certain chemicals named *fuel additives*. Thus, in order to get better some properties of fuels during storage, transportation, distribution and use, different additives are injected into fuels.

It is important to mention that sometimes oxygenates (ethers and alcohols) which are added to gasoline in large amounts (up to 15% vol.) are thought of as additives. They are not additives and are the competent components of gasoline (see Sect. 3).

Fuel additives are added in very small concentrations: from several ppm to several thousands ppm (1 ppm=0.0001 wt%). In such way, they are similar to corrosion inhibitors which also are added in small amounts in different media and significantly diminish their corrosivity. Usually such small amounts of additives are not reflective of the bulk composition of the mixture (fuels), but can significantly influence their properties. It is important that additives which improve some properties should not deteriorate other properties of fuels and its quality in general. Fuel additives are organic substances soluble in fuels (Appendix F). Some of these additives may help to maintain fuel quality (e.g., antioxidants, stabilizers, corrosion inhibitors, and biocides). Others may aid the movement of fuel through the distribution chain and into the vehicle tank (e.g., flow improvers, pipeline drag reducers, demulsifiers, and antifoams); may be added for legal reasons (e.g., dyes and markers) or can address specific concerns from motor manufactures (e.g., deposit control additives and lubricity improvers). We will describe fuel additives and how they work.

2.1 Action of Fuel Additives and Their Application

Use of gasoline fuel additives largely reflects developments in engines design and refinery operations, as well the problems occurring during storage and transportation of gasoline. Use of kerosene (jet fuel) additives reflects strict requirements to maintain properties of jet fuel. Use of diesel fuel additives reflects the impact of growing diesel fuel demand and the changing technology of diesel engines. Sometimes additives are divided according to the name of fuel: gasoline, jet fuel, diesel fuel and fuel oil additives. It is conditionally because the same additives (e.g., antioxidants and corrosion inhibitors) can be used in gasoline, jet fuel, and diesel fuel. Situation with aviation fuels (jet fuel and avgas) is unique in that only those additives specifically approved may be added to jet fuel. Before an additive can be approved for use in aviation fuel, it must undergo extensive testing to show both that it is effective and that it does no harm to any other fuel properties. To guard against harmful additive interactions, an additive must be tested at four times its maximum dosage in the presence of other additives before it is approved.

Antifoams All diesel fuels have a natural tendency to produce foam when pumped from a service tank into a vehicle's tank. This tendency is overcome by addition of polysilicone compounds.

Anti-icing additives Water in its liquid state is not only the cause of corrosion of metallic equipment and structures. In jet fuel or avgas, water turns into ice at temperatures below 0°C. Ice can form from dissolved water in fuel tanks at low temperatures during flights at high altitude. The freezing point of jet fuel is -47°C at pressure 1 atm. If free water is present in jet fuel, it will turn into ice at $T < 0^\circ\text{C}$ while the jet fuel is still liquid. The ice crystals can prevent fuel flow and possibly starve the engine for fuel. After the 1958 crash of a B-52 attributed to ice in the fuel, causing five of its eight engines to fail due to fuel starvation, anti-icing additives were introduced into military aviation fuels in the early 1960s.

To illustrate how the freezing point of water can be lowered, I describe three real-life incidents. In Siberia (Russia) in winter, where the air temperature was -45°C, I saw that car drivers did not use pure water for cooling their car engines. They added a solution called 'antifreeze', containing organic liquid alcohols—ethylene glycol or di-ethylene glycol—to their cars' cooling water in order to reduce the freezing point of the water used in their radiators. An 'antifreeze' is an additive (chemical compound) that lowers the freezing point of water. In Moscow's cold winters (the second example), I saw that table salt (NaCl) powder was dispersed on icy roads in order to lower the freezing point of water; namely, to turn ice into liquid water. Thus the ice combined with the salt turns into a liquid aqueous solution. The ice did not freeze at -5°C and even at -10°C to -15°C, and as a result, cars and people could move without danger of slipping, skidding, falling and accidents. The third example of use of de-icing solutions concerns flight in winter when the temperature is around 0°C. Once on a winter flight when I was inside the airplane, waiting to takeoff, I observed how de-icing (removal of snow, ice and frost from a surface) of both wings was done by spraying aircraft with a de-icing fluid. This fluid was based on propylene glycol, similar to ethylene glycol antifreeze used in some automobile engine coolants. Ethylene glycol is still in use for aircraft de-icing in some parts of the world because it has a lower operational use temperature than propylene glycol, but propylene glycol is more common because it is classified as non-toxic, unlike ethylene glycol. The de-icing solution not only de-iced the surface at the moment when it was applied, but also remained on the surface and continued to delay the reformation of ice for a certain period of time and prevents adhesion of ice. Hence, I was sure that our departure and flight would be safe. What is common between these three examples?

The freezing point of a solution is lower than that of a pure solvent. This phenomenon is based on thermodynamic properties of solutions. The decrease of a freezing temperature of a solution is proportional to the concentration of a solute (added substance) in a solution that is composed of ethylene glycol, propylene glycol or salt in an aqueous solution (2.1).

$$\Delta T_{\text{freez}} = T_{\text{freez}}^{\circ} - T_{\text{freez}} = i \cdot K \cdot m \quad (2.1)$$

where ΔT_{freez} is the decrease of freezing temperature of a solution; T_{freez}° and T_{freez} are the freezing temperature of pure solvent (water in this case) and solution respectively; i is a coefficient which shows electrolytic properties of a solute (how solute dissociates into ions in the solution), for instance, $i=1$ for non-electrolytes (ethylene glycol, propylene glycol and di-ethylene glycol among them), and $i=2$ for the table salt NaCl (if it fully dissociates into ions in water); K is the *cryoscopic* (*cryo* from the Latin means *cold*) constant which characterizes solvent (water in this case); m is the molality (concentration) of a solution (number of moles of a solute in 1 kg of a solvent).

According to (2.1) everyone can calculate the amount of a solute (for instance, ethylene glycol) in kilograms which must be added to water in order to diminish freezing point to any needed temperature. For instance, 3 kg of ethylene glycol must be added to 1 l of pure water in order that water will not turn into ice at -45°C . Certainly this solute must well dissolve in the solvent. Similar principle exists when anti-icing additives are injected into jet fuel, avgas or diesel fuel. They decrease the freezing point of dissolved water in the fuel. *Anti-icing additives*, or *icing inhibitors*, or *fuel system icing inhibitors* (FSII, pronounced “fizzy”) work by combining with water that forms solution and decreases the freezing of the aqueous solution so that no ice crystals are formed in the fuel. Anti-icing additives have hydroxyl groups (OH) in their structure which posses high affinity to water and long hydrocarbon chain for providing enough solubility in the fuel as well as prevention separation under temperature exploitation conditions. The first anti-icing additive in jet fuel was ethylene glycol (blue in color), but in the mid 1990s was changed to a clear di-ethylene glycol (exactly as in Siberia). The examples of FSII which are used today are di-ethylene glycol monomethyl ether (Di-EGME), ethylene glycol monomethyl ether (EGME) and isopropanol (IPA). Usually their concentrations are 1,000–2,000 ppm in fuels. These additives are slightly soluble in fuel but are very well soluble in water and its freezing point decreases to -60°C in the presence of additives. Anti-icing additives do not lower the freezing point of the fuel, only the water in the fuel. Unlike commercial and most Navy aircraft, Air Force aircraft do not have fuel heater systems to prevent moisture in the fuel from freezing. Water removes anti-icing additives from fuel, so introduction of water must be avoided. It is important to emphasize that the Di-EGME is also biocide and can be used for inhibiting microbiological growth in aircraft fuel systems, mostly *Cladosporium resinae* fungi and *Pseudomonas aureginosa* bacteria known as hydrocarbon utilizing microorganisms or *HUM bugs* (see Sect. 5.4). In fuels containing anti-icing additives, stagnant water bottoms can absorb large amounts of anti-icing additives. This aqueous solution with anti-icing additive can disarm water absorbing elements allowing water to pass down-stream. Therefore anti-icing additives are injected into jet fuel if it does not contain free water.

Anti-knock additives (Antiknocks) First, we will describe *knocking*. Normal combustion in a spark-ignition, internal combustion engine is initiated by a spark. The flame front fans out from the spark plug and travels across the combustion chamber rapidly and smoothly until almost all the fuel is consumed. *Knocking*, called also

detonation is the sound produced by abnormal combustion. Some of the unburned mixture components ignite spontaneously (auto ignites) and burns very rapidly. In other words, auto ignition is spontaneous ignition resulting in rapid reaction of the air-fuel mixture in an engine. The flame speed is many times greater than the normal ignition spark. In a reciprocating engine, the noise associated with auto ignition is called *knock*. *Knocking* due to auto ignition is also called *spark knock*. The resulting precipitous rise in cylinder pressure creates the characteristic *knocking* or *pinging sound*. Combustion is a very rapid series of chemical chain reactions between fuel vapors and oxygen. Factors that increase the rates of combustion reactions favor uncontrolled ignition (auto ignition) and knocking. These factors include higher temperatures, higher pressures, and more time after spark ignition. Anti-knock additives interrupt the chain reactions that lead to auto ignition (detonation). In order to evaluate the ability of gasoline to resist knocking as it burns in the combustion chamber *octane number (rating)* was suggested (see Sect. 10). Thus the *octane number* is an indication of gasoline quality, namely to “wait for the spark”. In the power stroke of a gasoline engine, the air and fuel is compressed by the piston before being lit by the spark plug, whereupon, it must burn smoothly. Hence, the gasoline must be capable of withstanding heat from the compression and radiation as the flame approaches, without spontaneously igniting. If the gasoline cannot withstand these effects, it explodes and this results in a characteristic ‘pinkish’ or ‘knocking’ sound from the engine. This is very dangerous as these explosions can cause loss of power, blast metals from the piston crown, or at worst, result in total engine failure.

The octane number scale is defined by two pure chemical reference fuels: normal heptane (*n*-heptane) with an octane number of zero (bad knock), and iso-octane (2,2,4-trimethylpentane) with an octane number of 100 (minimal knock). The selection of *n*-heptane as the zero point of the scale was due to its availability in high purity. This scale is arbitrary and is similar to Celsius temperature scale where zero temperature equals to freezing point of pure water and 100 temperature value equals to boiling point of pure water at the outer pressure 1 atm. Then were found substances with octane number higher than 100 (benzene, toluene, xylene, methanol, ethanol, ethers). The octane number of a blend of two reference compounds, *n*-heptane and iso-octane, is equal to the volume percentage of iso-octane it contains. A gasoline with an octane number of 96 has the same knock as a mixture of 96% vol. iso-octane and 4% vol. *n*-heptane. A fuel with a high octane number exhibits better resistance to auto ignition. Typical octane values for gasoline used in passenger cars are between 80 and 100. Of course, engineers searched for additives to gasoline in order to increase its octane number. On the chemical language, these additives had to increase activation energy of combustion of gasoline mixture. Activation energy is the minimum applied energy required to start chemical reaction (initiate combustion in this particular case). Injection of anti-knock additives allowed increasing activation energy of combustion which occurred smoothly (without detonation). Anti-knock additives were introduced in the 1920s to provide the octane rating needed to enable vehicle designers to increase engine compression ratios to levels which gave acceptable efficiency and performance.

Wide spectrum of anti-knock additives exists:

- a. Oxygenates: ethers—methyl tertiary-butyl ether (MTBE), ethyl tertiary-butyl ether (ETBE), tertiary-amyl methyl ether (TAME), di-isopropyl ether (DIPE); alcohols—methanol, ethanol, tertiary butyl alcohol (TBA) (see Sect. 3). Really they are not additives but components of fuels, because are added in large amounts (3% vol. methanol to 15% vol. MTBE).
- b. Aromatic hydrocarbons (aromatics): toluene, xylene, and benzene. The latter is toxic (including carcinogenicity) and therefore its amount is restricted by 1% vol. Maximum allowable concentration of aromatics in gasoline is 35% vol. These compounds possess similar problems like alcohol fuels, as they “eat” elastomer fuel lines (see Sect. 6.2) and has no lubricating properties as standard gasoline does, and thus can break down fuel pumps and cause upper cylinder bore wear.
- c. Aromatic amines: m-toluidine, p-toluidine, p-tert-butylaniline, technical pseudocumidine, N-methylaniline, and cumidines. They were used in avgas during World War II.
- d. Organometallic compounds (carbonyls): methyl cyclopentadienyl *manganese* tricarbonyl, *iron* pentacarbonyl, and ferrocene (*iron* dicyclopentadienyl). Like the first anti-knock additive tetra-ethyl lead (TEL) is based on Pb, these additives also are based on metals Mn and Fe.

Each of them has benefits and disadvantages. Nowadays most spread anti-knock additives are oxygenates and aromatics (see Sect. 3).

Antioxidants (inhibitors of fuel oxidation) Gasoline, jet fuel and diesel fuel contain unstable unsaturated hydrocarbons (olefins and diens) which can polymerise and form gums. The gums are carried forward into the engine system, and can lead to its malfunctioning and breakdown. In addition, olefins and diens containing in gasoline react more readily with dissolved oxygen than the other classes of hydrocarbons. This is a paradox of our being, because life on Earth requires oxygen for its existence on the one hand, and from another hand oxygen is a highly reactive molecule that takes part in many unwanted processes. Oxygen oxidizes tissues of living organisms, metals, and fuels. The chain of oxidation reactions can result in formation of hydroperoxides (ROOH) and peroxides (ROOR') in fuels. They are highly oxidizing agents resulting in increase of corrosiveness of gasoline (see Sect. 1.2.1.2). Such problems (to stabilize the fuel and reduce the tendency for gum to form) can be avoided by injection of antioxidant chemicals. An antioxidant is a molecule that inhibits the oxidation of other molecules. A freshly-cut apple turns brown because of oxidation. If you spray lemon juice on exposed fruit or vegetable (e.g., avocado), these fruit and vegetable will not be oxidized because the lemon juice is an antioxidant.

Oxidation can produce free radicals which can start chain of oxidation reactions in fuels. Antioxidants work by interrupting this chain of reactions (removing free radical intermediates), preventing the formation of hydroperoxides, peroxides, soluble gums, or insoluble particulates. Antioxidants do this by being oxidized

themselves instead fuels. Antioxidants are often reducing agents, such as hindered phenols, aromatic amines and diamines, or mixtures of aromatic diamines (e.g., phenylenediamines) and alkyl phenols. Antioxidants became more important in the 1970s when increased the concentrations of olefin compounds in fuels. Antioxidants are the biggest gasoline additives. They are also used in aviation gasoline, jet fuel, diesel fuel, and biofuel (see Sect. 4). Prior to now antioxidants were injected as close as possible to producing of fuels at oil refineries. However, nowadays it is clear that nothing to hurry to inject them. It is possible to compare use of antioxidants in fuels with their function in living organisms (ascorbic acid or Vitamin C) and in corrosion of metals (corrosion inhibitors).

Antistatic additives When I was a child I saw many times how gasoline tankers moved on the road and metallic chain which was at the back of the tanker loudly drag along the asphalt. Why do gasoline tankers usually have metallic chains at the back? The metallic chain is supposed to get rid of any static electricity that builds up within the vehicle by directing it from the tankers into the ground or road. Preventing the buildup of static electricity excludes the possibility of a spark occurring if somebody happens to touch the unit. Gasoline is highly flammable, and its vapors are explosive, and the spark can provide an ignition source. When fuels (e.g., gasoline, jet fuel or diesel fuel) move through a pipe, hose, valve, filter, or storage tank, static electrical charge can be generated (see Sect. 5.3.1).

The Greek philosopher Thales of Miletus discovered about 2,500 years ago that, when rubbing fur against a piece of amber, a static force that would attract dust and other small particles to the amber was produced which now we know as the 'electrostatic force'. The same phenomenon happens because two dissimilar surfaces (liquid fuel and solid surface of pipe or other object) move across each other and one of them (hydrocarbons containing in fuels) has very low electrical conductivity (non-conductors): 1–50 CU (conductivity unit) (see Sect. 5.3.1). When electrical conductivity of fuel is lower than 1 CU, it is practically does not charged. Such fuel is characterized by high purity but it is difficult to reach and keep. Thus, rapidly flowing liquid that is a relatively poor electrical conductor (like fuels) can result in a static charge being created much faster than it dissipates. The rate at which the static charge dissipates is proportional to the liquid's ability to conduct electricity (electrical conductivity) (see Appendix F). When electrical conductivity of fuel is greater than 50 CU, static charge dissipates enough quickly, and electrical charge is not accumulated. Thus 50 CU is a minimum value in order to prevent accumulation of static electricity. When the accumulated charge exceeds the ionization electric potential (measured in volts) of the air above the liquid, it can discharge from the liquid surface as a spark. The energy of the spark can initiate an explosion if the liquid is flammable and the composition of vapor and air in the vicinity is in the flammable region. In order to prevent such explosions, three measures are used: earthing (bonding and grounding), pumping rate limits, and time for charge dissipation (relaxation time), before the fuel is exposed to air. Another measure is to inject some substances to fuels for increasing their electrical conductivity and charge dissipation. Therefore they are called *conductivity improving additives*, or

antistatic additives, or *static dissipater additives*, or *electrical-conductivity additives*. The chemicals used are fuel-soluble chromium substances, polymeric sulphur- and nitrogen-containing compounds, and quaternary ammonium salts. One of such additives, Stadis 450 (composed of 8 ingredients), is used at 3–5 ppm in jet fuel and avgas. When additives are used, the conductivity of the fuel must be between 50 and 450 CU. Use of antistatic additives reduces the hazard of electrical charge accumulation. These additives do not prevent charge generation; they increase the rate of charge dissipation by increasing conductivity of fuels. In other words, static dissipater additives aid in relaxing static charges and decrease the possibility of fires or explosions caused by static electricity. It is mistake to think that all additives (antistatic between them) have no deleterious effect. For instance, antistatic additive ASA-3 in concentrations 1–3 ppm has been used in jet fuel for many years. It comprised three compounds (chromium salt of an alkylated salicylic acid, calcium di (2-ethylhexyl) sulpho-succinate and organic polymer) which can serve also as a surfactant and a dirt disperser. Its use in combination with corrosion inhibitor revealed harmful effect on the coalescence ability of filter separator. Of course, its manufacture was stopped. Therefore it is important to examine all possible side-effects of new additives.

Anti-valve seat recession additives The lead additive (TEL), in addition to its primary purpose of increasing octane number, also provides a critical wear-reducing function by depositing a thin protective layer of lead salts on valve seat surface. Without this protection, exhaust valve seats wear or recede into the cylinder head. After banning of use of TEL in 1990s, the problem of wear appeared. The problem of valve seat recession is overcome by the use of chemicals based on potassium, phosphorous and manganese salts. The combusted metal salts act as a protective lubricant and prevent the direct metal-to-metal contact that would otherwise cause high wear.

Biocides (see Sects. 5.4 and 7.5) Most microorganisms which include bacteria and fungi (yeasts and molds) that live in the water 'love' hydrocarbons containing in kerosene (jet fuel) and diesel fuel. Thus liquid hydrocarbon fuels represent an excellent nutrient source. Microorganisms can be air or waterborne. Microorganisms 'love' heavy hydrocarbons (C_{16} and higher) containing in jet fuel and diesel fuel more than light hydrocarbons containing in gasoline and naphtha. When water appears in jet fuel or diesel fuel, the microbes begin to proliferate at the interface water-fuel. Detrimental action of microorganisms on fuels appears as deterioration of fuels, in biofouling, clogging of filters, and corrosion of metals contacting fuels. Certain fuel additives, especially those rich in nitrogen and phosphorous, encourage microbial growth. As a result the additives are degraded and their effect is lost. Biocides are substances that kill microorganisms. They also are called *antimicrobial agents*. Biocides are used in every aspect of life: from toiletries to air conditioners, drinking water and swimming pools. Certain sulphur organic compounds containing in conventional kerosene and diesel fuel are natural biocides. The desulfurization processes at the oil refineries make low sulphur kerosene and diesel fuel, and natural biocides are no longer present in enough quantities to kill microorganisms.

Biocides using in crude oil and fuels are organic substances composed of boron compounds (substituted dioxaborinanes), isothiazolines and ethylene glycol (injecting in fuels); 2-Bromo-2-nitropropane-1,3-diol, glutaraldehyde and heterocyclic compound based on thiadiazine-2-thione (injecting in aqueous phase contacting with fuels); some ethers and quaternary amines (injecting in diesel fuel). Since most biocides are toxic and dissolved in aqueous phase, any water bottoms that contain biocides must be disposed of appropriately.

Detrimental action of microorganisms on fuels appearing in biofouling, clogging of filters, deterioration of fuels, and corrosion of metals became beneficial when microorganisms are used in bioremediation. Bioremediation is the use of microorganisms to remove pollutants (in this case fuels are pollutants).

Cetane improvers The diesel engine does not contain a spark plug. It is a compression-ignition engine and relies on the diesel fuel to auto-ignite to begin combustion. The diesel fuel ignites after it is mixed with the hot air toward the end of the compression stroke of the engine. Ignition delay is the time between injection of the fuel into the cylinder and the onset of combustion. If the delay is too long, combustion is more violent (and hence noisier) and less efficient (causing high levels of exhaust emissions and poor fuel economy). This ignition delay is explained by the fact that there is no time for fuel to pass needed preparation for engine with ignition from compression. This preparation is accompanied by accumulation of peroxides which initiate auto-ignition. Thus intensity of oxidation, delay of ignition and the temperature of auto-ignition of diesel fuel depend on its chemical composition. Normal alkanes and alkenes are oxidized with large rate and at lower temperatures than aromatic hydrocarbons. Therefore the presence of normal alkanes and alkenes is desired as they provide shorter induction period during oxidation of fuels in the engine, and oxidation products (hydroperoxides) provide lower auto-ignition temperature, easy start and gentle work of the engine. In order to estimate an ability of diesel fuel to auto-ignite, we should choose two compounds: one of the best ability and another of the worst one to auto-ignite under compression. The first compound chosen is hydrocarbon alkane hexadecane ($C_{16}H_{34}$) named *n*-cetane, a liquid that ignites very easily under compression. It was given a base rating of 100. Another reference is alpha-methylnaphthalene ($C_{11}H_{10}$) with a value of 0. *Cetane number* represented the volume percent of *n*-cetane in alpha-methylnaphthalene that ignites similarly to the diesel fuel being measured. In 1962, because of difficulties in handling alpha-methylnaphthalene and its expense it was replaced with more stable compound heptamethylnonane (a C_{16} isomer isocetane). The latter was assigned a cetane rating of 15. *Cetane number* is the measure of how well diesel fuel ignites. Similar to the octane number rating that is applied to gasoline to rate its ignition stability, *cetane number* is the rating assigned to diesel fuel to rate its combustion quality. Engines operating on diesel fuels with a low cetane number are difficult to start, especially in cold weather, noisy, emit high levels of white smoke and hydrocarbon pollutants at start up, produce less power and consume more fuel. The greater amounts of alkanes, alkenes and naphthenes, and fewer amounts of aromatics are in diesel fuel the higher its cetane number. Diesel engines operate well with a cetane

numbers from 40 to 55. Not all diesel fuels have such values. In order to increase cetane number, namely, to initiate the oxidation of the fuel in the engine in liquid phase before the formation of vapor-air mixture and thus accelerate the formation of hydroperoxides and as a result to provide gentle, uniform and stable combustion in the engine, various additives are injected. These additives are alkyl nitrates (e.g., 2-ethyl-hexyl nitrate, octyl nitrate, iso-propyl nitrate, amyl nitrate) and di-tert-butyl peroxide. They initiate oxidation of cycloalkanes (naphthenes) and aromatics containing in large amounts in diesel fuels, breakdown during combustion to form free radicals, which increase the rate of decomposition of the hydrocarbon components of fuel, reduce ignition delay, and thus facilitate the start of engine.

Combustion chamber deposit modifiers All spark-ignited engines develop combustion chamber deposits. These deposits are formed as a result of condensation of partially-thermally oxidized hydrocarbons of gasoline and additive components on the relatively cool piston and cylinder head surfaces. Organic polyetheramines and compounds containing combination of a saturated carboxylic acid and an alkylated or alkoxyated amine are such additives for controlling (preventing or reducing) combustion chamber deposits in engines.

Corrosion inhibitors Corrosion of carbon steel tanks, pipes, and other equipment containing gasoline and naphtha occurs because of dissolved water and oxygen (see Sect. 5.3). Other aggressive compounds, such as elemental sulphur, hydrogen sulphide, mercaptans, disulphides, low molecular weight carboxylic acids and oxyacids can cause corrosion in diesel fuel and jet fuel. The more fuel is purified from corrosive sulphur- and oxygen- containing compounds and isolated from atmospheric oxygen and water vapor, the less its corrosivity. Free water appearing in fuels during their storage is especially corrosive because of organic low molecular weight corrosive compounds are dissolved well in this free water and become corrosive. Microorganisms also find favorable food and conditions for their proliferation at the interface water-fuel. Even if elemental sulphur, H_2S and mercaptans are absent in fuels, they may appear as a result of break-up of complicated organic sulphur-containing compounds. *Corrosion inhibitors are substances which are added in small amounts for decrease or prevention corrosion of metals.* High molecular weight carboxylic acids, aliphatic amines with long chains, the amine salts of carboxylic acids, aliphatic polyamines and polyamides are used as corrosion inhibitors of carbon steel in contact with fuels. These organic compounds are the polar molecules that adhere by the charged part to the metal surface and form the protective film which does not allow water, oxygen and other corrosive components reach the metal surface. In addition, carboxylic acids can react with iron and form nonsoluble salts on the carbon steel surface which also prevent the penetration of corrosive species and their further contact with the steel surface. Thus mechanism of protection may be adsorption or chemical reaction of inhibitors with metal surface. Corrosion inhibitors were introduced in 1940s and can be added to gasoline, jet fuel, and diesel fuel. Their concentrations are ranged between 5 to 100 ppm in gasoline, and 450 ppm in diesel fuel. Aliphatic amines are efficient corrosion inhibitors of carbon steel and copper alloys in both hydrocarbon and aqueous phases. Organic



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