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FUEL ADDITIVES AS A SOLUTION TO CHEMMOTOLOGICAL PROBLEMS

A. M. Danilov

The emergence and growth of research on fuel additives, dictated by technology improvements and toughened ecological standards, are discussed. Leading experts in this field and key Russian scientific schools and their contributions to the development of domestic additives and import substitution are mentioned. Prospects for new developments are outlined.
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Additives are often the optimal solution to problems associated with the production and use of fuels [1]. Alternative means tend to be unworkable or uneconomical. The first problem to be solved using additives was the production of antiknock aviation and then automotive fuels. Starting in 1919, xylidine was added to aviation fuels in the USA and England; up to 4% extraline (*N*-methylaniline), in the USSR. The unique antiknock properties of tetraethyllead (TEL) were discovered in a General Motors laboratory in 1921. It began to be used in the USSR in 1936 when production for the army started at the chemical plant in Usolye-Sibirskoe (in 1938, at the Oka Plant in Dzerzhinsk). TEL was not used commercially for a long time and was approved only in 1956 with the limitation that ethyl gasoline could not be used in Moscow, Leningrad, capitals of USSR republics, resorts, and the Far North.

The toxicity of TEL forced researchers to seek safer additives. On one hand, a theory of knock was developed; on the other, mass screening was carried out. Both approaches yielded results. Lerner [2] in Russia attempted to generalize them and showed that the antiknock effect could be represented as a periodic function of the nuclear charge of the additive metal. Alkali metals could be expected to have high antiknock effects. Mavrin [3] in Russia attempted to develop this idea by synthesizing lithium compounds that were

All-Russian Research Institute of Oil Refining. e-mail: Dafi_pris@mail.ru. Translated from *Khimiya i Tekhnologiya Topliv i Masel*, No. 5, pp. 31 – 34, September– October, 2014.

very soluble in fuels. However, these efforts were not developed because a ban on metal-containing additives to light fuels soon appeared.

Screening gave spectacular results. Ferrocene was discovered by the analytical chemist Poson in 1951 and was quickly tested successfully for antiknock effectiveness. Antiknock agents based on it were developed around the world. This research was carried out at several USSR institutes, in particular, at I. M. Gubkin Russian State University of Oil and Gas under the direction of T. P. Vishnyakova. Other metallocenes were also studied. Almost all of them, especially those containing manganese, were effective antiknock agents. However, the drawbacks of metallocenes nullified their advantages. Effective carriers like for lead were not found for iron and manganese. Sparkplugs fouled and deposits formed in combustion chambers if those additives were used. Furthermore, several such compounds were light-sensitive. As a result, extraline was re-examined. However, although extraline was formerly technical *N*-methylaniline with impurities of aniline and *N*,*N*-dimethylaniline, *N*-methylaniline of 97% purity with added antioxidant Agidol-1 began to be used.

Several institutes and well-known companies in Russia investigated alternative antiknock agents. Technology development was centered at the All-Russian Research Institute of Oil Refining, where a variety of industrial additives were created under the direction of V. E. Emel'yanov. This allowed production of ethyl gasoline to be completely stopped in 2002. The work was awarded an RF Government Prize in 2003.

In 1937, 4-methyl-2,6-di-*tert*-butylphenol, which was discovered during a search of possible antioxidants, was patented by Standard Oil under the trade name Ionol. It became the platform for a large family of antioxidants based on sterically hindered phenols, which are still widely used in fuels and lubricants. Ionol production in the USSR began at the Novokuibyshevsk pilot plant and at the Sterlitamak petrochemical plant in 1970, where a variety of sterically hindered phenol antioxidants are still produced.

Systematic research on various types of fuel additives started in the USSR during the middle of the 20th century. The first monograph reviewing the foreign and domestic results was the book published in 1959 by Sablina and Gureev, scientists at Research Institute No. 25 of the Ministry of Defense [4].

The problems with gasoline were solved temporarily. However, problems with the gel point of diesel fuels remained unsolved. Drivers were forced to heat automobile tanks by building small fires under them before hitting the road. The solution seemed obvious. Depressor additives based on alkylphenols and alkylnaphthalenes, which prevented the growth and aggregation of *n*-paraffin crystals, were used successfully in lubricants in 1931. Unfortunately, all attempts to use these additives in diesel fuels were unsuccessful. It was commonly thought that depressors were in principle unsuitable for fuels. It was discovered only after several years of persistent research that the mass and structure of the additive played a decisive role. These parameters should correspond in a certain manner to the size of the paraffins and the shape of the crystals formed by them. It was found that many known polymers, e.g., polyolefins, polyalkylacrylates, and their copolymers, provided the desired effect. More-or-less available polymethacrylates and ethylene-vinylacetate copolymers were produced first. The latter were preferentially marketed for a number of reasons. Research resulted in the creation of an enormous variety of this type of additive. On one hand, this was explained by the great synthetic potential of polymers and copolymers and, on the other, to the practical need. The depressor action turned out to be so selective for different petroleum products that an additive with unique physicochemical characteristics had to be selected for almost each case. The problems with using fuels at low temperatures in the USSR were reviewed in detail in the monograph of B. A. Englin [5].

Basic research in Russia on depressor additives for petroleum products was centered at the All-Russian Research Institute of Oil Refining under the direction of R. A. Terteryan [6]. The technology for synthesizing ethylene-vinylacetate copolymers at comparatively low pressure (10-15 MPa instead of the traditional 100 MPa) was developed. This technology was implemented at the Angarsk Catalysts and Organic Synthesis Plant, where separate batches of depressors for boiler and diesel fuels are currently manufactured. The efforts of Terteryan were further developed by his coworkers S. T. Bashkatova (PDP additives) [7], F. V. Oktyabr'skii (DMN-2005 additives), and A. M. Bezgina (a series of DMN additives).

Another problem with diesel fuels was their poor flammability in the combustion chamber of high-speed engines. This problem was acute in countries that added low-octane fractions from secondary processes to commercial fuel. This problem affected the D. I. Mendeleev Yaroslavl and Komsomol'skii naphthene petroleum refineries in the USSR. The IPN (isopropylnitrate) additive was developed for them in the 1970s using an existing feedstock base. 2-Ethylhexylnitrate, which is less hazardous and simpler to produce, was used exclusively for this purpose abroad. 2-Ethylhexylnitrate is currently manufactured at Ya. M. Sverdlov (Dzerzhinsk) and Biisk Oleum Plants. Work on improved alkylnitrate technology and new additive development is continuing simultaneously at Oksokhimneft' Ltd. (G. N. Novatskii and B. G. Sokolov).

Exhaust gases containing products from incomplete gasoline combustion and nitrogen oxides came under scrutiny in the second half of the 20th century. Engines and fuel systems were improved. In particular, automobiles were equipped with positive crankcase ventilation (reburning of crankcase blowby vapors, a mixture of unburned fuel and oxygen) back into the engine. This decreased by 20% the emission of unburned hydrocarbons but created harsh conditions for the carburetor. The carburetor throttle operated poorly and stopped regulating the combustion mixture after only 10-15 thousand km because of fouling. The engine lost power. Use of specially developed detergent additives enabled the mileage of an automobile to be more than doubled. The first additives of this type were developed by Chevron in 1954. Analogous additives in Russia were developed at the All-Russian Research Institute of Oil Refining under the direction of I. S. Korsakova. The additive Afen and its modifications were based on fatty-acid amides and polyalkylenepolyamines. They entered the retail market and were used where needed upon inspection by the automobile owner.

The American engineer and industrialist E. Houdry proposed in 1948 the use of catalytic conversion to improve the economics and ecological characteristics of power plants and engines. His device was based on a catalyst deposited on aluminum oxide or another support attached to a ceramic or metal substrate. Oxidation (combustion) of carbon monoxide and hydrocarbons and reduction of nitrogen oxides to molecular N_2 or NH_3 through the action of hydrocarbons occurred on the catalysts. The predominance of some reactions or others depended on the catalyst and mixture composition. It was established that the optimum effect was achieved if the excess air coefficient was strictly constant and close to unity. The carburetor, being an analog device, was incapable of such fine tuning. However, electronic systems for controlling the combustion mixture composition were invented to fill the gap. The carburetor was eliminated from the fuel supply system. The calculated amount of gasoline was fed directly into the intake manifold through input valves and injectors.

Then, the injectors and input valves needed detergent additives. The injectors were located very close to the combustion chamber where the temperature reached 180-400°C. Moreover, not pure fuel but that mixed with spent gases (recirculation of spent gases reduced nitrogen oxide emissions by 20-30%) was fed into the cylinder through the injectors. Traditional detergent additives were ineffective in this instance and even worsened the situation because they decomposed at high temperatures. The next crisis in engine construction and the need to return to old designs were discussed. The required additives were found and were based on so-called polybutenes and polyesteramines, which are used in large volumes abroad and also in Russia. A domestic additive of this type, called Kaskad-9, was developed at Plastneftekhim Ltd. It was allowed for use in producing ecologically improved gasolines at Moscow Refinery.

Another factor that affected the development of new fuel additives was the rigorous standards for sulfur content in all fuel types. Diesel fuel lost its lubricating and antistatic properties starting with a sulfur content of about 0.035 mass%.

This was not a new problem for additive developers. Antiwear additives that effectively protected the rubbing surfaces had been used for a long time in tribological practice. A large variety of such additives was developed for greases. Additives for reactive fuels also existed. Problems with wear began to arise in supersonic aviation. Fuel in tanks experienced aerodynamic heating to 200°C and sometimes 250°C during flight at 2-3 Mach. Fuel was extensively hydrogenated in order to remove traces of resins and heteroatomic compounds and to increase the thermal stability. However, the antistatic, antiwear, and anticorrosion characteristics of the fuels worsened markedly. Additives were again called into question. The requirements for them were very strict but the selection was limited. However, the required developments appeared rather quickly in Russia. Naphthenic acids isolated from Baku crude with high naphthene contents began to be used as antiwear additives. The group at Research Institute No. 25 of the Ministry of Defense (B. A. Englin) together with specialists of the All-Russian Research Institute of Oil Refining developed an additive that was called K.

Deflagration and explosions occurred during pumping and filtering of hydrogenated reactive fuels. Discharges of static electricity that was formed during friction of the dielectric (fuel) with the apparatus walls were responsible. Antistatic additives ASP-1 and ASP-2 based on chromium salts of carboxylic acids were used in industrial processes (work with resinous glues and rinse liquids). These were unsuitable for reactive fuels because they caused carbonization in the engine. New developments were needed. Thus, Sigbol, a composition of chromium complexes of synthetic fatty acids with an alkylmethacrylate-methylvinylpyridine copolymer, appeared. It was just as effective and even better than foreign analogs. It was created by two groups at I. M. Gubkin Russian State University of Oil and Gas (I. F. Krylov) and the All-Russian Research Institute of Oil Refining (E. M. Bushueva).

However, new developments were required in order to improve the antiwear properties of diesel fuels. Additive K did not pass a water-compatibility test. Furthermore, its feedstocks were in a foreign country after the dismantling of the USSR. The feedstock for Sigbol also turned out to be scarce. Therefore, research on restoration of the lost variety was started at the All-Russian Research Institute of Oil Refining. In particular, the additive Baikat was developed and implemented. It captured a significant part of the domestic market for antiwear additives. A second domestic additive for this application is also noteworthy. This is Kompleksal-Eko D (original name Kaskad-5), which was developed at Plastneftekhim Ltd. [8].

In addition to the All-Russian Research Institute of Oil Refining, a successful scientific school in the area of fuel additives was assembled at I. M. Gubkin Russian State University of Oil and Gas under the direction of T. P. Vishnyakova (O. P. Lykov, I. F. Krylov, and I. A. Golubeva). This group developed the antioxidant Agidol-12, metal deactivators, biostatics, etc. [9].

Our article would be incomplete if we did not mention current problems. As before, they are related to either technology development or ecological standards. With respect to technology development, it is necessary to mention first of all ramped diesels with the Common Rail fuel injection system. In essence, fuel is fed into a common line, the ramp, where it is under constant pressure and injected into the combustion chamber under computer control. As a result, the pressure in the combustion chamber rises rather smoothly. The system can save up to 20% of the fuel. However, the fuel in this engine is under a pressure of 250 MPa, in contrast with the traditional engine (10-40 MPa). The very severe conditions cause increased wear and coking of the injectors. The optimal way to solve these problems is to use multi-functional additives. However, known additives are ineffective because they do not tolerate the very severe conditions under which modern diesel fuel systems operate.

Biofuels present problems just as serious. This is primarily ethanol for gasolines. Tanks containing mixtures of gasoline and ethanol corrode 1-2 orders of magnitude faster than those with only petroleum-based gasoline. Many known antirust additives are unsuitable. New developments are being made abroad. It was reported that effective candidates were obtained. In Russia, this area is beginning to be developed at the All-Russian Research Institute of Oil Refining under the direction of V. E. Emel'yanov.

In conclusion, we note that Russia often lags behind industrially developed western countries with respect to fuel additives. Many additives are imported. Such a situation occurred in the 1990s when domestic developers were unprepared for the new standards. Now, rather successful groups of developers are being formed and are capable of creating a domestic variety to replace imports. In 2013, 30% of the demand for antiwear additives was met by domestic producers; 70%, for deflagration promoters. Work is continuing on the creation of new depressor and antistatic additives.

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