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Fuel Additives - Todey And Tomorrow

RESEARCH

With systematic researches of fuel contents one can see that its components are resistant differently against detonations (differently not explosive). So the aim was to produce the components with higher resistance against detonations and to increase considerably their percentage in the fuel. So, neither automotive industry nor mineral oils industry, which main activity was firstly transport and refining of crude oils, could find practical solution for "detonation" problem. In this written it is shown that the answer to this question lies in fact that metal organic compound Bleitetraethyl [tetraethyl lead Pb $(C_2H_5)_4$] verzy efficiently avoid detonation.

Keywords: *aditives, benzine, engine, detonation*

1. INTRODUCTION

Although people are familiar with oil for thousand of years, its industrial preparation and application started in the middle of the last century. First of all, petroleum was produced from oil in refineries and it was used as lamp oil. In that process, a kind of liquid was produced as a secondary product that could not be used for that purpose due to its low boiling point. The liquid was called "petrol" in Germany, later it was sold as agent for cleaning in pharmacies. Later on, when the German engineer Nicolaus Otto invented "otto engine" in 1876 and 10 years later when Carl Benc from Mannheim produced the first car, petrol was not in the "shadow" any more.

The first car in a series of produced cars was a "Benz-Velo" car that in 1888 was hailed as "a complete replacement for a vehicle drawn by horses". A contemporary wrote the innovation as follows: "Horse`s vivacity became its main flaw. Engine on oats (horse) has one major fault: it consumes even when it does not work, besides, its bones cannot be welded".

At the very beginning a car did not affect mobility of a man. The first cars reached an average speed of about 15 km/h, unless any failure in function would end carlier its rides. In 1901 Baudry de Saunier, an author of one of the first books on cars, wrote the following: "Almost all failures are caused by the engine". Considering today`s point of view it is hardly surprising, since the engine development was in its cradle, and the used fuel-petrol that was sold in pharmacies, it fulfilled its new purpose partly.

Hardly had the first cars been driven out of production workshops, their designers had already worked on the improvements. Their principal target was to increase the power, and later other criteria such as comfort and reliability became important.

In 1910 there was a revolutionary discovery on the car development: the engine power was increased considerably by an increase of the mixture compression fuel-air in it. But soon the starting euphoria decreased. However, it was found out that increase of fuel compression, being available at that tiime, brought to uncontrolled increase of pressure. Self-ignition of the fuel-air mixture that is similar to explosion, so called "Klopfen" ("detonation"), caused failure of engine. Soon it was noticed that the problem could not be solved with the technical replacement of the engine but with replacement of fuel only. In other words: lack of fuel quality was an obstacle for its technical innovation.

With systematic researches of fuel contents one can see that its components are resistant differently against detonations (differently not explosive). So the aim was to produce the components with higher resistance against detonations and to increase considerably their percentage in the fuel. However, every refinery may vary the content of its products within certain limits. But the refinery technology in that time was not suitable to solve the problem. So, neither automotive industry

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nor mineral oils industry, which main activity was firstly transport and refining of crude oils, could find practical solution for ”detonation” problem. It was the matter of competence and only chemistry offered the solution.

Relative resistance to detonation

Origin	Components	Relative efficiency
Refinery	• Toluene	1,1
	• iso-Octane	1,0
	• iso-Butane	0,35
Chemistry	• MTBE	2,0
	• Tetraethyl lead	17 000

Figure 1.

In this stage an invention of an American chemist was shown as a direction for fuel development. In 1922 it was found that a metal-organic compound Bleitetraethyl [tetraethyl lead Pb (C2H5) 4] avoided the detonation very efficiently, when it included free radicals which were produced during combustion. Since this effect overcomes the most effective refine components for more than 17000 times, the fuel resistance against detonation can be increased drastically, with the traces of tetraethyl lead (figure 1). It was birth of the fuel additive.

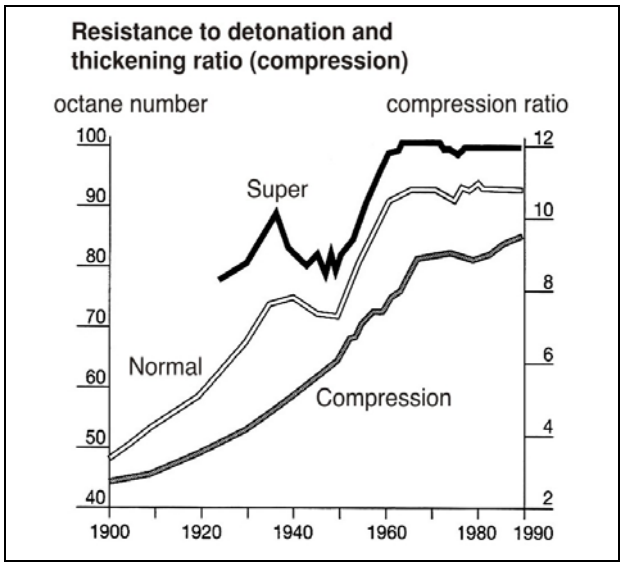

Figure 2.

No engine power improvement could be realized in the following decades without any improvement of the fuel resistance against detonation (figure 2). Besides decisive impulses for development of engine and fuel came from the car races sports, firstly from aviation. Here the power and reliability were decisive and it may be said that they were essentially decisive criteria. Without help of the science this development was not possible.

2. NO PROGRESS WITHOUT ADDITIVES

A huge increase of number of cars (figure 3) faced very early the mineral oil industry to another problem that, up today, it requires increased funds for investments and research: preparation of large quantities of fuel and in the same time estimation of less valuable secondary products resulted from their manufacturing.

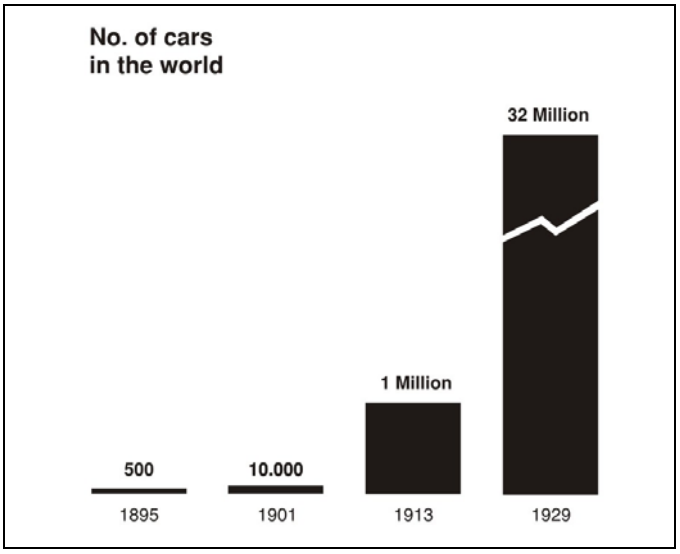

Figure 3.

In 1920 the need for petrol exceeded the capacity of refineries in those days. Therefore a new method of refining had to be developed. Indeed, it was successful that, wiith the help of new fission, the utilization of used petrol components was increased and in the same time a number of components increased in petrol being resistance against detonation (not explosive). Besides, new processes of fission gave unstable components and therefore decreased stability of petrol at storage.

This problem was also solved. A new class of additive, the antioxidant, was developed. These additional substances psrevent or retard the process of petrol aging (caused by oxygen), reaching the creation of polymer residues. And today antioxidant is also an important integral pppart of the fuel.

Tetraethyl lead and antioxidant are two examples for fuel additives, the substances that in smaller quantities- less than one percent - are given to the refined products to improve the quality.

Above mention sampples are characteristics for whole development of cars and fuels. Lead tetraethyl and antioxidants are the examples for fuel additives, which are, in fact, substances added in small quantities - less

than 1 % - to the products of refining in order to improve their quality.

The mentioned examples are characteristic for overall development of cars and fuels. The development of the latter had to follow continually the improvements made in the development of engines, which demanded not only the fuel of higher quality but also the more quantities at more favorabble prices.

In addition to that, the number of additives kept rising from the beginning of 1920-ies (figure 4). The development of car industry contributed to the improving of technology of car and fuel production.

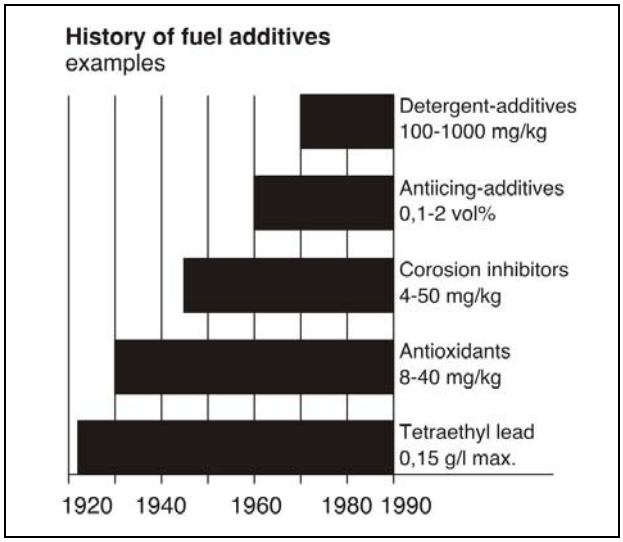

Figure 4.

3. DETERGENT - ADDITIVES, EXAMPLE OF THE LATEST TECHNOLOGY

The mass motorization and crisis with petroleum after II World War had a strong influence upon the car development. Beside the former primary objective - improving of power - some new requests occurred, such as reduction of substances in exhaust gases, which are hazardous for environment, and saving of resources.

Upper limits regulated by legislation in 1980-ies and greater competition in automotive industry caused the pace never seen before in the engine development process. The application of energy was significantly improved, as well as the behavior of engines regarding the exhaust gasses. However, at the same time, engines became more sensitive to disturbbances and more complex. Lead tetraethyl, the first additive, was redrawn from the market. Even without this largely accepted additive the quality of fuel had to be adjusted according to new requests. Automotive industry developed non-expplosive compponents, such as methyl - tert.-butilether. (MTBE)

Today refineries produce basic fuels according to the standards determining the minimum requirements. These basic fuels are complex miixtures, usually with over 200 components, which are made of several types of raw petroleum in various refining processes. So, from the aspect of chemistry, each type of petrol has a completely different composition. However, basic petrol always contains certain critical substances - without regard to nature of raw pppetroleum and the process of making.

Riding vehicles on basic fuel, thast is with fuel without additives, after several thousands kilometers will result in occurrence of precipitation of something similar to coke in the intake system. These precipitations increase fuel consumption and exhaust emission. And they effect the power and shorten the engine life time.

In order to avoid all this automotive industry developed detergent - additives. Their molecular structure and their effect are the same as for tensides (surface active materijal). They wash away the organic remainders from surfaces of intake system in engine and they form a protective layer which prevents this precipitation. (figure 5)

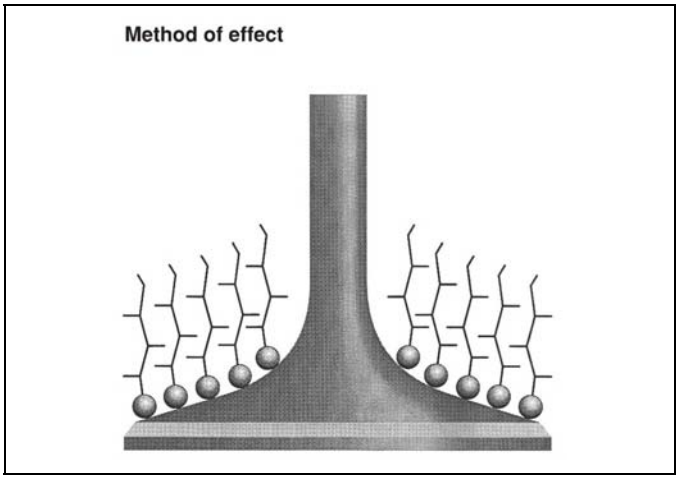

Figure 5.

These additives must meet many requirements:

- The smaller the quantity the greater the efficiency,
- Similar to medicines, they must not have bad side effects,
- In all fuels and types of vehicles, under various working conditions, they must fulfill their main function

Since there are a number of variables in this engine and fuels system, it is not unexpected that the costs

of development of detergent-additives amount to those of making new medicine.

This field of work is present worldwide with various competent bidders, such as: BASF, SHELL, CASTROL, BP, VALVOLINE, TOTAL, LF, LUKOIL and ZASTAVA. As part of "Zastava automobili", "Rezervni delovi" (spare parts deparatment) and Central Laboratory in cooperation with BASF, continually conduct the researche work whose aim is to increase the efficiency of additives. Depparatment for development (in Central Laborataory) has one engine on which we conduct tests and which is used continuously.

After twenty yeas of detergent-additives developppment, a class of chemical substance meeting complex requirements emerged. It was long-chained hydrocarbons with amino groups (figure 6). Parts of these carbons usually contain polyisobutenes.

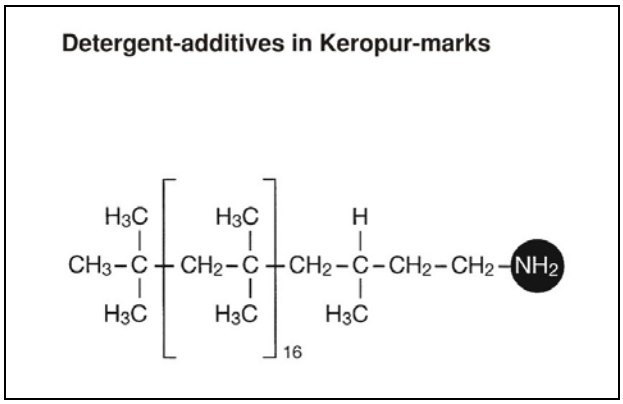

Figure 6.

Detergent-additives are used, not according to the motto "It helps a lot and we need it in large quantities", in precise doses. Its concentration today is approximately 200 ppm. One tons of petrol contains about 200 g. of additive, that is one spoonful of additive per one fuel tank. Costs amount to 0,1 EURO per one liter.

When considering the fuel quality, detergents are the basic characteristic of fuels, despite their small concentration; they are so called "vitamins and minerals" of petrol. Most customers are completely unaware of this fact. Since unions of mineral oils, for cost sake, often change basic fuels, technology of additives is very often the only characteristic by which we can tell the difference between various producers. In 1970, some politicians charged with fraud a fuel producer who highlighted in advertisement some positive effects of his additive. On the other hand, in 1994 Federal Deparatment for Environmental Protection praised the increased application of additives. From 1995, a "Clean Air Act" came into effect and according to it additives should be added to all fuels.

Fuel additives protect environment and are very useful for consumers:

- Additives reduce the fuel consumption for exactly 4%.

So, when annual fuel consumption in Western Europe is 120 millions tons the reduction of CO_2 emission amount to over 8 millions tons. Today, out of these possible 8 millions tons of reduction 60% is reached. In Eastern Europe and Asia the percentage of additives share in fuel is significantly lower.

- Additives reduce exhaust emissions. Carbon-monoxide emission is reduced approximately in 15%, while hydrocarbon and nitrogen-monoxide emissions in 10%. These figures are rather great, when we bear in mind that annual carbon-monoxide emissions, conditioned by fuel consumption, in Western Europe amount to 4,7 millions tons, the emissions of hydrocarbon amount to 600 thousands tons per year, and of nitrogen-monoxide 1,1 millions tons per year.

Aral`s study from 1994. Estimates that the total national application of additives in fuels in Germany is about 8,6 billions DM per year. The use of additives in fuels saves each driver 1.000 DM per year.

4. MAKING OF DETERGENTS WITHOUT CHLORE, INNOVATION MADE BY BASF

BASF took an active part in all phases of additives development. With a range of innovations it had a crucial influence upon the development of modern detergent additives. This is not surprising, because these additives are systems of polymers containing functional groups, and the analyzing of polymer functions is their specialty. All methods for making of detergent-additives used so far include chlore. BASF aimed at producing detergent-additive without chlore, and at finding an environmental friendly way of uniting these two characteristics. First, using polymerization of clear isobutene without chlore, they made a new highly reactive polyisobutene (figure 7).

This turned out to be a success. Today, only BASF and BP Chemicals are capable to produce technically satisfactorily highly reactive polyisobutene. Using this method we can introduce nitrogen without chlore. As a result we get polyisobutenamine with greater efficiency than previous products. All the research work was conducted in BASF, but according to the mutual agreement with ZASTAVA, it is at disposal of ZASTAVA experts and it is applied to the following

products: ZASTAVA PROTEKT PLUS I (for diesel passenger cars), ZASTAVA PROTEKT PLUS II (for trucks), and ZASTAVA BENZIN PLUS (additive for petrol). All these products were tested in laboratory by BASF - Germany and WYANDOTTE - USA, and appproved by relevant European Union Council.

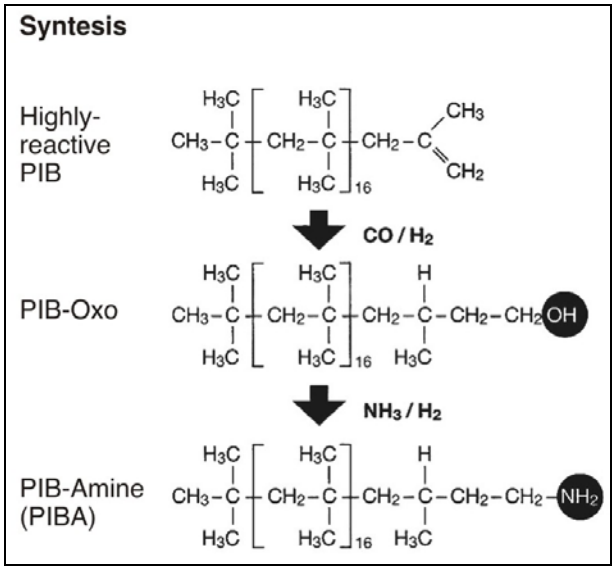

Figure 7.

5. REQUIREMENTS SET FOR THE FUTURE

There are over five hundred millions registered cars in the world. According to the study made by World Bank, in 15 years there will be about 8 hundred millions. In Germany, on 1000 residents there are 500 passenger vehicles, while in India and China that number is less than 10. 15% of world population own 80% of cars. Up to 2010, we expect that this percentage will rise in Asia first and then in other regions. At the same time, the concern for the pollution of environment grows, because, in the near future, the fossil energy carriers, because of their energetic content, will remain an important source of raw materials for petrol. It is sure that it will remain an important source of raw materials for petrol. It is sure that it will be possible to reduce significantly the specific emission because of continual further development of automotive technology and fuel quality. The same rules go for the development that will happen in the future as for the development which took place in the past:

- Optimizing of energy consumption,
- Saving resources,
- Minimizing emissions

One thing is for sure: without help of science it is not possible to economically produce fuels of necessary level of quality, which is a task full of responsibility, that can be solved only in cooperation with car producers, mineral oils industry, additive suppliers and legislators. ZASTAVA has great predisposition to contribute significantly to fulfilling of this task.

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