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Research on the effect of the effective microorganisms, silver solution and colloidal nanosilver addition on the engine oil base number (TBN)

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In the article, base number as a parameter characterizing the washing and dispersing abilities of engine oil were characterized. Next, the influence of additives enriching engine oils on the natural environment was described. In the further part of the article, the research methodology, applied oil samples with additives of effective microorganisms and silver solution, both for fresh oil and used oil were presented. In addition, the measuring test stand with instrumentation and measuring device was shown. In the main part of the article base number value for fresh and used oil compared to oils with the addition of microorganisms and a solution of silver and colloidal silver were described. Next the analysis of the influence of these additives on the base number value was made. The article was completed conclusions.

Key words: *petroleum products, base number value, ennobling additives, effective microorganisms, silver solution*

1. Introduction

Crude oil, or rock oil, is the most important hydrocarbon raw material for the production of valuable industrial products, such as gasoline, diesel oils, lubricating oils, paraffin. Among hydrocarbon products, lubricating oil, diesel and biodiesel (blends of fatty acid methyl esters with diesel fuel) that are used in diesel engines are the most susceptible to microbial degradation. Such a decomposition occurs even in the case of properly operated engines. The condition for the growth and development of numerous - bacteria and fungi in these products is the presence of organic carbon compounds and water [3, 6]. Hydrocarbon products are characterized by the ease of adsorption of water particles at the interface, hence it is a common pollutant. Many species of bacteria and fungi have the ability to grow in petroleum products that are a source of carbon and energy. Therefore, the life activity of microorganisms causes the decomposition of hydrocarbons and refining additives and the release of water, sulphur compounds, surface-active substances to the fuel. The result is changes in the chemical composition of the fuel and the value of some physical parameters, such as boiling point, base number or viscosity.

In this study the impact of the effective microorganisms, silver solution and colloidal nanosilvers addition on the fresh and used engine oil base number was analyzed [4].

2. The base number as a parameter characterizing the washing and dispersing abilities of engine oil

Modern engine oils are technologically advanced products that meet stringent requirements in terms of physicochemical properties and actual performance.

The parameters characterizing lubricating oils include, among others. viscosity, volatility describing the tendency of an oil to evaporate at high temperatures. Then it is the Total Base Number (TBN) of the so-called reserve of alkalinity in the oil (TBN is the ability of the oil to neutralize the acid products of combustion). The alkalinity buffer is used to neutralize the acids formed as a result of oxidation processes, especially fuel combustion, especially in the case of using low-quality fuel with high sulfur content and oil oxidation. The amount of acid in the oil is described by another number known as the Total Acid Number (TAN), measured according to ASTM D 664. As the oil ages, the TBN value gradually decreases as the TAN increases. At some point, these values become the same, which is known as TBN/TAN point crossover (Fig. 1). In this situation, the protection of the engine against corrosion deteriorates significantly and an oil change is necessary. Unless poor quality fuel is used and oil change intervals are adhered to, it is unlikely that there will be a TBN/TAN break-off point. In most cases, particle contamination, not acidity, is the main cause of an oil change [2, 10].

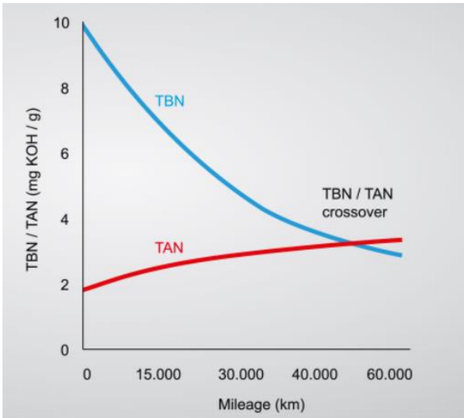

Fig. 1. Change in the value of TBN and TAN depending on the oil mileage [1]

3. The impact of additives enriching engine oils on the natural environment

The preparation of high-quality engine oil is no longer possible just by using advanced base oils. Contemporary lubricating oils consist of two basic groups: base oils and a package of enriching additives.

The use of an oil base and refining additives of petroleum origin in the content of lubricants is associated with a negative impact on health and the environment [5].

Lubricating oils with additives cause serious damage to soils, due to the multistep physicochemical processes leading to a change in the forms and distribution of organic matter, in the range of carbon, water, nitrogen, and phosphorus. As soil is an environment for a variety of microorganisms and higher living organisms, its contamination with petroleum-based lubricants becomes hazardous and a detrimental effect on biological life may occur. The proper functioning of the ecosystem may be disturbed. Mineral oil can clog pores in the soil, resulting in reduced aeration and water infiltration. The presence of petroleum compounds may reduce or limit the permeability of soils, and, consequently, cause the degradation of soils due to oxygen deficit [1, 7].

One of the additives are biocides, which are pesticides used, inter alia, to combat or limit the growth of microorganisms in petroleum products. They should have a broad spectrum of activity on various groups of microorganisms, dissolve in the aqueous and organic phase, be effective at low concentrations and efficient in use. It is very important to dose the biocides correctly. Too small amounts may result in the immunization of microorganisms and, consequently, the use of ever higher doses to ensure the expected effectiveness. It is not without its impact on the natural environment, because most biocides also destroy beneficial organisms and cause unfavorable changes in the composition of microorganisms. Despite the number of benefits resulting from the use of biocides, there are currently strong tendencies to limit their use [6]. They are caused by the fear of the harmful effects of these highly concentrated substances on the environment [8, 9].

One way of combating microorganisms with regard to environmental aspects can be effective microorganisms (EM), that is, a complex of cultures of beneficial naturally occurring microorganisms, genetically unmodified, remaining in a state of equilibrium, not only harmless to humans, animals and the environment, but even necessary for their proper functioning.

Another environmentally friendly compound is nanosilver, i.e. microscopic particles. Thanks to the fragmentation of silver into nanoparticles with a size of 1 to 5 nm, the effectiveness of using the bactericidal, fungicidal and virucidal properties of silver has increased incomparably. Crushed silver to nanoparticles has a disproportionately larger active surface, and thus a previously unattainable biocidal potential. The effectiveness of nanosilver includes the elimination of over 99.99% of bacteria, fungi, viruses and mold. Nanosilver is able to attach to bacterial cell membranes and block their production of enzymes necessary for reproduction and growth.

Therefore, as part of research work with the use of the effective microorganisms and silver compounds, their influence on, among others, the base number of lubricating oil was investigated.

4. The research methodology

In the conducted tests, the base number of engine oil was measured. For this purpose the Titrator TitroMatic 2S has been used (Fig. 2).

TitroMatic 2S titrators are equipped with two exchangeable burettes. Additionally, the titrator used for the tests is equipped with a peristaltic pump for automatic dosing of reagents, mediating in the analysis process and automatic determination of the sample volume before titration.

In this titrator, the movement of the piston of the digital glass burette (piston) is provided by a precise stepping motor with a resolution of 1/40000 steps. For a 10 ml burette, the maximum dispensing resolution is 0.00025 ml and ensures a real minimum dispensing accuracy of 1 µl (0.001 ml). The dosing precision of the titrator is compared with the accuracy of the analytical balance [11].

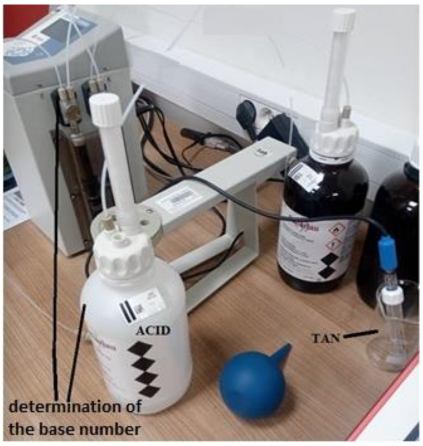

Fig. 2. TitratorTitroMatic 2S device prepared to determine the base number

The tests were carried out using samples of the 5W30 fresh and used motor oil according to the ASTM D 2896 standard. Each sample was tested three times and the final result is the mean of these measurements.

One of the additives which improve the properties of oil are effective microorganisms. They are specially selected the smallest organisms on Earth. It is a composition of 81 different strains of aerobic and anaerobic microorganisms, incl. lactic acid bacteria, yeast, photosynthetic bacteria and actinomycetes. This technology was developed by Teruo Higa, Professor of Horticulture at the Agricultural Academy of Ryukyus University in Okinawa, Japan. In trade, effective microorganisms exist in liquid form and as ceramic tubes. EM ceramic tubes are clay fermented with effective microorganisms and then fired under special anaerobic conditions. Effective microorganisms preserved in a ceramic form are characterized by the fact that they are resistant to high temperatures and maintain their beneficial properties for a long time. Effective microorganisms have a pH of 3.5.

The second addition was non-ionic and ionic silver. Non-ionic silver, i.e. colloidal silver (research studies used silver with a concentration of 25 ppm and pH 6–8). Colloidal silver is 80% of silver particles, while the remaining 20% are silver ions. It has a yellow color because the silver particles that are dispersed in the water block the light passing through them. Ionic silver is silver solution (research studies used silver with a concentration of 37 ppm and pH 6–8). Ionic silver is as transparent as water. Ionic silver contains 90% silver ions and only about 10% silver particles. As 90% of the particles are silver ions, a more appropriate name is "silver solution".

Samples have the addition of the effective microorganisms in liquid form in the amount of 2.5 ml and 5 ml and ceramic tubes in the amount of 3 pieces and 6 pieces. In addition, silver solution and colloidal nanosilver in the amount of 2.5 ml and 5 ml to fresh and used oil were added. In addition, fresh oil and used oil without any additives were also tested to compare the base number obtained.

In order to measure the base number, the device was first calibrated by recognizing buffer solutions with known pH values. After calibrating the device, a titration was made. First, a blank test was made, pouring 100 ml of solvent Mixture T.A.N. After this test, 20 ml of oil of known weight was poured in. After these activities, electrometric titration with hydrochloric acid solution HCl was carried out. After the end of the titration, the weight of the tested oil was entered and then the base number in mg/KOH was obtained, which was determined to be equivalent in terms of acid neutralization ability to the alkaline additives contained in 1 g of improved lubricating oil.

5. Results and analysis of tests

In order to analyse oil base number changes for each samples, the test results are presented in the form of graphs in Figs 3–6. These graphs show different values of the base number after adding to fresh and used oil effective microorganisms in liquid form (2.5 ml and 5 ml per 100 ml of oil) and in the form of ceramic tubes (3 pieces and 6 pieces with a diameter of 9 mm and a height of 11 mm for 100 ml of oil). In addition, silver solution and colloidal nanosilver were added to fresh and used oil in the same proportions as for effective microorganisms (2.5 ml and 5 ml per 100 ml of oil).

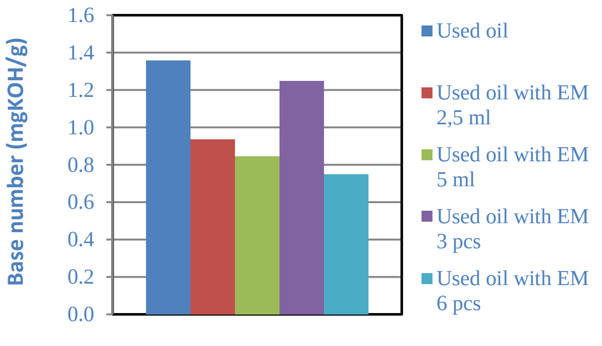

Fig. 3. Base number of used oil and used oil with EM in liquid form and ceramic tubes

Analysing the above results, it can be seen in Fig. 3, that for used oil the base number is 1.358 mgKOH/g, while the addition of the effective microorganisms to the oil in the amount of 2.5 ml and 5 ml causes the base number to drop to 0.937 mgKOH/g and 0.844 mgKOH/g, respectively, which means more greater deterioration of oil properties. On the other hand, adding microorganisms to the oil in the form of ceramic tubes in the amount of 6 pieces also reduces the base number to the value of 0.749 mgKOH/g, which is not favorable for the oil, but for the amount of 3 pieces of these tubes, the smallest decrease occurs, to 1.250 mgKOH/g. In general, the addition of any amount of the effective microorganisms to the used oil deteriorates the properties of the oil, reducing the already low base number.

In the case of adding 2.5 ml of colloidal nanosilver to the oil, a slight decrease in the base number to 1.350 mgKOH/g can be observed (Fig. 4), i.e. it can be concluded that this amount of silver addition neither improved nor deteriorated the properties of the oil. It looks different when adding 5 ml of colloidal nanosilver, because in this case there was a slight increase in this number to 1.402 mgKOH/g. As for silver solution, this additive significantly reduced the base number, both with the addition of 2.5 ml and 5 ml, to 1.037 mgKOH/g and 1.199 mgKOH/g, respectively, which means that it adversely affected the properties of the oil. From this it follows that adding any additives to the used oil does not improve the properties of the oil, and even makes them worse. The oil behaves as if it were the higher mileage than it actually is.

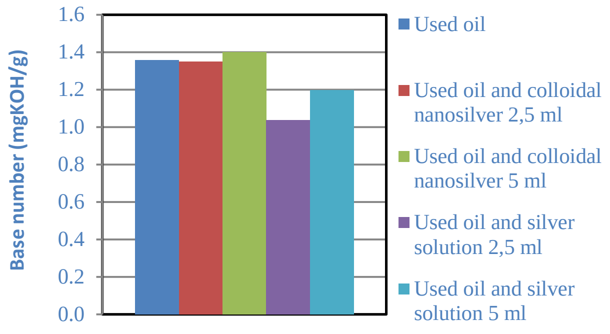

Fig. 4. Basenumber of usedoil and usedoil with colloidalnanosilver and silversolution

The base number for fresh oil (Fig. 5) is 3.907 mgKOH/g, while the addition of 2.5 ml and 5 ml of the effective microorganisms in liquid form reduces the base number to 3.606 mgKOH/g and 3.444 mgKOH/g, respectively. As a result, such oil will require earlier replacement with a new one, as its degradation will occur faster. The higher the amount of this supplement, the more the acid value is reduced.

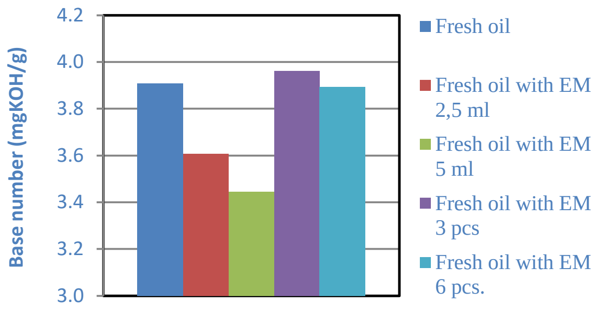

Fig. 5. Base number of fresh oil and fresh oil with EM in liquid form and ceramic tubes

The addition of EM to fresh oil in the form of ceramic tubes causes an increase of the base number to the value of 3.962 mgKOH/g with the addition of 3 pieces of ceramic tubes, while 6 pieces basically does not change the value of the base number. In general, it is worth adding EM ceramic tubes to the fresh oil and see how it reduces this number during the operation of the combustion engine.

The addition of fresh colloidal nanosilver in the amount of 2.5 ml and 5 ml to the oil resulted in a significant reduction of the base number to the value of 3.604 mgKOH/g and 3.7551 mgKOH/g, respectively, while the addition of silver solution in the same amount as colloidal nanosilver also reduces the base number, thus together to a value of 3.479 mgKOH/g and 3.731 mgKOH/g.

In this case, it should be noted that for both silver solution and colloidal nanosilver additions, a greater decrease in the base number occurs with a smaller amount of this additive, a greater amount caused a smaller decrease in the base number. Therefore, it is worth checking the addition of silver ions to fresh oil with even more added to the oil than in previous studies.

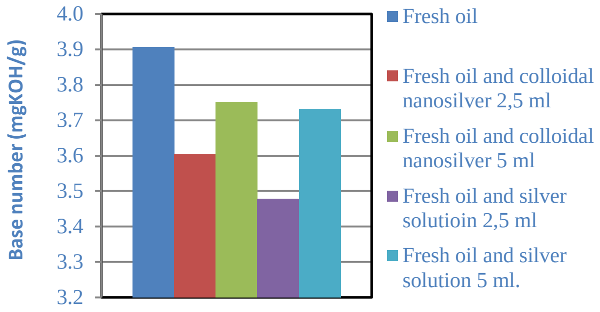

Fig. 6.Base number of fresh oil and fresh oil with colloidal nanosilver and silver solution

6. Conclusion

The aim of the research was to test the effect of the addition of the effective microorganisms and silver solution and colloidal silver on the base number of used and fresh oil. Adding any amount of EM to the used oil worsens the properties of the oil, reducing the already low base number, although for three pieces of ceramic tubes the smallest decrease occurs.

The addition of collidal nanosilver and silver solution to the oil also does not favorably affect the value of the base number. Only the addition of colloidal silver in the amount of 5 ml causes a slight increase in the base number, but it is not significant enough to improve the properties of the oil. In general, adding any additives to the used oil does not improve the properties of the oil, and even causes them to deteriorate. The oil has parameters as if it were the higher mileage than it actually is.

The situation is different in the case of adding EM and silver to fresh oil, because the addition of effective microorganisms in the form of a liquid reduces the base number, which will cause such oil to require an earlier replacement with a new one because its degradation will occur faster.

The greater the amount of this addition, the number of base lowers more. On the otherhand, adding EM to freshoil in the form of ceramic tubes increases the base number of freshoil, which may have an impact on the reduction of this number during the operation of the engine. Too many tubes does not have a positive effect on the value of this number.

Moreover, for the addition of silver solution and colloidal nanosilver to the fresh oil, a greater decrease in the base number occurs with a smaller amount of this additive, a greater amount resulted in a smaller decrease in the base number. Therefore, it is worth checking the addition of silver ions to fresh oil with even more added to the oil than in previous studies.

Nomenclature

TBN total base number
TAN total acid number
EM effective microorganisms
HCl hydrochloric acid
KOH potassium hydroxide

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