Article citation info:
Krakowski R. The effect of adding effective microorganism and silver compounds to flash point of engine oil. Combustion Engines. 2023;192(1):97-104. https://doi.org/10.19206/CE-153001

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The effect of adding effective microorganism and silver compounds to flash point of engine oil

ARTICLE INFO

Received: 23 June 2022
Revised:3 August 2022
Accepted: 25 August 2022
Available online: 2 October 2022

The article presents the effect of the effective microorganisms and silver compounds addition on the flash point of new and used oil. The work describes environmentally friendly additives to engine oil. Next the ignition point of the engine oil were described. In the further part, the research stand and methodology were presented. In the main part of the article the flash point values for new and used oil compared to oils with the effective microorganisms and silver compounds addition were shown. New and used oil samples were mixed with effective microorganisms in the form of a liquid (2.5 ml and 5 ml) and ceramic tubes (3 pcs and 6 pcs). In addition, silver solution and silver compounds were mixed in the same amounts as the liquid effective microorganisms. In summary it was stated, that adding of the effective microorganisms to the fresh oil in liquid form causes the flash point to drop significantly. It follows that effective microorganisms in liquid form have a very negative effect on the properties of the oil. In the case of microorganisms in the form of ceramic tubes, which in this larger amount slightly increase this point compared to oil without additives. Regardless of the type of silver and its quantity, very low flash point values were obtained. For used oil the best results are obtained with the addition of microorganisms in liquid form. For the used oil the addition of silver compounds does not have the beneficial effect of restoring the original properties.

Key words: *engine oil, flash point, oil properties, effective microorganisms, silver compounds*

1. Introduction

Currently an increasing influence, in connection with the tightening of regulations on the emission of toxic compounds and carbon dioxide (CO_2) into the atmosphere, have alternative drives that are under intense development. Nevertheless, internal combustion piston engines, including marine engines, are still developed and improved to meet these stringent standards [3, 4, 6, 8, 11, 18].

Due to its design, the operation of the piston engine is not possible without a properly selected lubricating oil. Lubricating oil is an integral part of any internal combustion engine and must meet all the design requirements set by the engine constructor [2, 17, 22].

As a result of work in the engine, the oil undergoes the processes of oxidation, aging and destruction. The oil oxidation products and aging create sludges, carbon deposits and varnishes that change the physicochemical properties of the oil and are highly corrosive to metal parts of the engine. In order to counteract these phenomena, the oil is mixed with additives. One of them are biocides that are harmful to the environment. Therefore, additives are currently being sought that will fulfill this role at the current level and will be environmentally friendly [1, 7, 9, 20, 23].

For this purpose, it was decided to check the effect of the addition of effective microorganisms and colloidal silver on the value of the ignition point of engine oil. The flash point is the lowest temperature at which airborne oil vapors can ignite on contact with a flame and should be as high as possible because it affects oil consumption. So it is very important to check that these additives will not deteriorate the properties of the oil in this regard. The flash point is another parameter investigated because the influence of these additives on the acid number, base number and viscosity of the engine oil [12–14] was previously investigated. These studies show that it is worth conducting research in this direction, with better results improving the properties of the oil obtained for effective microorganisms than for nanosilver. For used oil, it is better to add microorganisms in liquid form, and to new oil, microorganisms in the form of ceramic tubes, from which they are slowly released into the engine oil. As for nanosilver, the results were similar for used oil and new oil, which shows that the addition of silver does not have such a positive effect on the improvement of oil properties as effective microorganisms.

The article presents the research results for new and used oil with and without the addition of effective microorganisms and silver compounds as oil enriching agent to slow down the process of microbiological degradation of lubricating oil [21].

2. Engine oil and additives improving the properties of the oil

The primary task of the oil is to lubricate the moving parts of the engine over a wide temperature range. This is done by creating a durable and break-resistant oil film. Its role is to separate the mating engine parts from each other and reduce the friction coefficient, which will significantly reduce the wear of mating engine parts. This function is related to the viscosity of the oil, i.e. its ability to separate the cooperating elements from each other. Immediately after starting the engine, the oil should reach all friction nodes and create an oil film of appropriate thickness and strength. At the same time, its continuity must be maintained in order to prevent even point contact of the mating metal parts.

The second very important function of engine oil is heat dissipation, which is especially important in modern turbocharged combustion engines. Due to the fact that some engine components can reach very high temperatures, the task of the oil is to extract large amounts of heat from them. For this reason, a high flash point of the lubricant, adequate temperature stability and protection against oxidation at high temperatures are important.

A very important function is to keep the engine clean, which has a positive effect on the technical condition of the engine. The oil prevents the build-up of low- and high-temperature contaminants that remain dissolved in the oil. It is important to properly add improvers so that the oil does not become the cause of its degradation due to, for example, increased microbial contamination that may occur in petroleum products. For this reason, an important element is the prevention and protection of petroleum products against microbial contamination. Such protection may include physical methods such as settling, fuel filtration or thermal decontamination, and a chemical method. Physical methods are less burdensome to the environment, but unfortunately their use is limited. For this reason, other agents are used, which include biocides, i.e. compounds of synthetic or natural origin. Biocides are pesticides that are used, inter alia, to combat or limit the growth of microorganisms in petroleum products. Xbee cleaners are also used in the storage of petroleum products to help eliminate water, reducing deposits such as rust [43, 44].

Due to the fact that physical and thermal methods are ineffective, and chemical methods use highly concentrated substances that have a detrimental effect on the natural environment, it is necessary to develop effective, environmentally friendly methods of combating the phenomenon of microbiological contamination of fuels and oils. These methods should take into account both technical aspects and the specificity of the processes taking place in the fuel and lubricating systems [15].

One of such measures may be effective microorganisms, that is, specially and properly selected smallest organisms on Earth. The composition of 81 different strains of aerobic and anaerobic microorganisms (Fig. 1), incl. lactic acid bacteria, yeast, photosynthetic bacteria, mold or actinomycetes. It was developed by Professor of Horticulture Teruo Higa from the Agricultural Academy of Ryukyus University in Okinawa, Japan. According to the creator, properly and systematically introduced into the environment give it the potential of biodynamic self-renewal and regeneration [10, 27].

Photosynthetic bacteria using available conditions, eg CO_2, temperature, produce useful biochemical active compounds from organic matter or toxic gases. Lactic acid bacteria also slow down the growth of harmful bacteria. Another important component of the mixture is yeast. Thanks to fermenting mushrooms, organic matter is decomposed and unpleasant odors are neutralized. The principle of operation of EM is based solely on natural processes, they are not genetically modified and completely environmentally friendly [16, 18, 19, 34, 35, 37, 40].

Another environmentally friendly measure can be the use of silver. This chemical element has long been used for protective and healing purposes. Silver is also used in filters, as well as to clean the air of microbes and water in closed spaces, e.g. in airplanes. The silver ionization method contributed to the enhancement of the disinfecting effect of this element. Silver ionization, like copper ionization, has found application in the elimination of some bacteria [5, 32]. Silver is also used in the form of nanosilver.

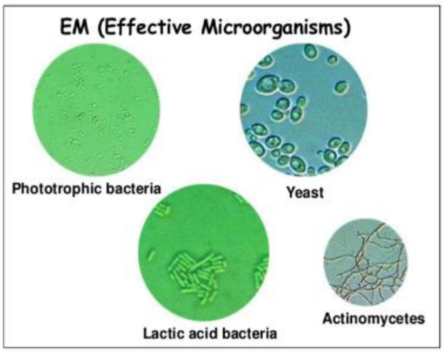

Fig. 1. A composition composed of various strains of aerobic and anaerobic microorganisms that are part of effective microorganisms [39]

Nanosilver is microscopic particles - silver ions that can only be observed through an electron microscope. 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.

3. Flash point as one of the parameters characterizing engine oil

The flash point for oil is the lowest temperature at which an oil sample develops sufficient vapours under specified conditions for the air-vapour mixture above the sample to ignite for the first time without continuing to burn afterwards. If the oil-air mixture burns for at least five seconds or longer, this is referred to as the focal point of the oil. The focal point is usually only a few degrees Celsius above the flash point. The flash point alone is not a sufficient quality feature of oil, nor does it allow conclusions about the suitability of the oil. Moreover, they cannot be drawn on the subject of oil consumption in internal combustion engines. The flash point is an important constant for any type of lubricant, therefore each oil is tested for its flash point. The flash point contributes significantly to the scope of the lubricant application. Each oil has a different flash point. Depending on the application, a certain flash point may also be required. Basically, it can be said that the flash point of paraffin-based oils with a density between 860 and 890 kg/m^3 is between 200 and 280°C. For naphthene-based oils with a density between 890 and 960 kg/m^3 flash points of 235°C and lower are reached [24, 25, 36, 38].

In the case of engine oils for passenger cars, flash points of 200°C to 270°C are usually achieved. Some special oils for industrial applications can reach flash points above 300°C.

Particularly in combustion engines, the oil may mix with fuel after prolonged periods of use, resulting in oil dilution. The entry of foreign substances, fuel or water is also the reason why the flash point of other oils could drop. If the flash point of the oil sample falls below 150°C, the oil should be changed to reduce the risk of fire.

As shown in Table 1, flash points for conventionally refined mineral oils can range from 165°C for an ISO 22 viscosity oil to a high 260°C for an ISO 1000 viscosity oil. Flash points also vary somewhat within viscosity grades as influenced by the crude oil type and refining process [33].

Table 1. Typical flash points of industrial lubricants [33]

Oils ISO VG	Flashpoint	
	^{o}C	F
22	165	329
100	224	435
150	226	439
220	232	450
320	236	457
460	236	460
680	238	460
1000	260	500

As previously mentioned, synthetic lubricants typically exhibit higher flash points than their mineral-oil counterparts. Therefore, it is sometimes possible to detect a wrong or mixed oil with the use of flash point testing. However, from a practical standpoint, other routine tests such as infrared spectroscopy, TAN viscosity and color are more effective in alerting users to wrong or mixed lubricants. In these instances, the flash point test better serves in a confirming role.

4. The research stand, materials and metodology

5W30 synthetic oil was used for the tests, which slightly changes its viscosity during temperature changes. As a result, it perfectly lubricates engine parts, while protecting it against deposits of carbon deposits, sludge and other harmful impurities that can accelerate its wear. At the same time, the specificity of 5W30 oil allows it to maintain its fluidity even at very low temperatures, which significantly facilitates engine start-up in winter.

The new oil had a dynamic viscosity at 2^{o}C at the level of 598 mPa·s, while at 63^{o}C (the maximum temperature obtained on the viscometer), it was 26 mPa·s. In addition, the flash point was measured, which is 212.44^{o}C.

Used oil, the same type as the new one, i.e. 5W30 synthetic, was also used for testing. This oil was used in a compression ignition engine under variable conditions and had a mileage of approx. 15,000 km.

The dynamic viscosity of the oil at 2^{o}C is 697 mPa·s, while at 63^{o}C – 24.5 mPa·s, additionally, the ignition point was measured, which was 198.8^{o}C.

Before starting the research, effective microorganisms and silver were added to the oil about 4 weeks earlier.

Figures 2 and 3 show samples of new oil, new oil with additives and used oil. In the case of used oil, the color and appearance were the same no matter what additives were added.

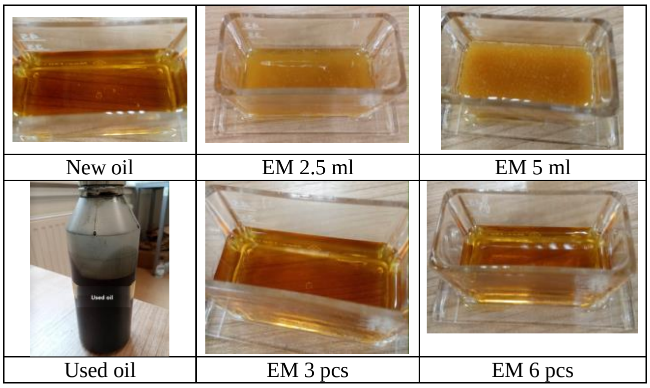

Fig. 2. Fresh oil, with the addition of effective microorganisms in liquid form and ceramic tubes and used oil

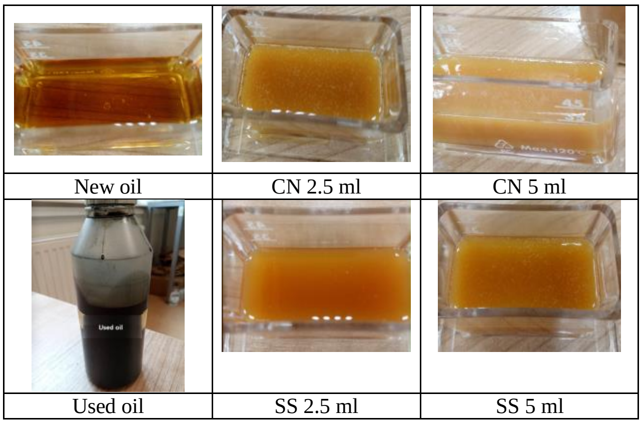

Fig. 3. Fresh oil, with the addition of silver solution (SS) and colloidal nanosilver (CN) in liquid form and used oil

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) was added to fresh and used oil.

Effective microorganisms of the commercial form presented in Fig. 4 were used for the research.

Fig. 4. The commercial form of effective microorganisms in liquid form and ceramic tubes [29, 31]

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). Nanosilver was used for the tests in the commercial form shown in Fig. 5.

Determination of the flash point for new and used oil using an automatic apparatus for testing the flash point in a closed crucible – EraFLASH was carried out (Fig. 6). The device advantages are the speed and precision of determinations, the patented technology of heating and cooling from –25°C to +420°C (in one apparatus), and the applied methods of determination according to the standards: ASTM D 6450 and D 7094.

Fig 5. The commercial form of colloidal nanosilver and silver solution [26, 30]

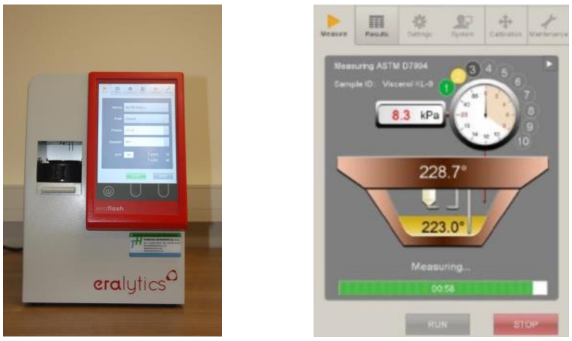

Fig. 6. Apparatus for testing the flash point in a closed cup – EraFLASH [41, 42]

ERAFLASH is a device that enables the measurement of the flash point for all types of fuels, such as diesel oil, fuels, biofuels, solvents, fragrances and flavors, paints, varnishes, residual fuels, marine fuels, tars, asphalts and solid substances. The apparatus can also be used to determine the degree of fuel dissolution in the engine oil. Besides, it is easy and convenient to use also in the field.

A small amount of sample: 1 ml for the ASTM D 6450 method or 2 ml for the ASTM D 7094 method and the crucible closed during the test, guarantee the highest safety for the laboratory. The sample is heated in the closed measuring chamber from above. An electric arc is used for ignition. This device uses neither open flame nor electric filament. The flash point is measured as the point where the pressure of the gases in the measuring chamber increases rapidly. The use of small samples reduces the costs of collecting, storing and disposing of samples and beakers after analysis, and also facilitates the cleaning of the device [28].

As for the tests of the samples that were used to make the graphs and analysis, they were carried out in accordance with the ASTM D7094 standard.

5. Results and analysis of research

In order to analyse oil flash point for each samples, the test results are presented in the form of graphs in Figs 7, 9, 11 and 13. These graphs show the variation in the value of the oil's flash point after adding to fresh and used oil effective microorganisms in liquid form and in the form of ceramic tubes. In addition, silver solution and colloidal nanosilver were added to fresh and used oil in the same proportions as for effective microorganisms. Each sample of pure oil and oil with additives were tested three times. However, the article presents the average result for each case.

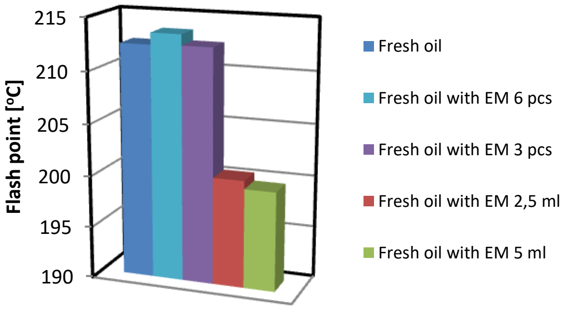

Fig. 7. Flash point oil of fresh oil and fresh oil with EM in liqiud form and ceramic tubes

Analyzing the results obtained, it can be seen in Fig. 7, that for fresh oil the flash point is 213°C. On the other hand, adding of the effective microorganisms to the oil in the amount of 2.5 ml causes the flash point to be lowered to 200°C, while the greater amount of liquid additive, i.e. 5 ml, lowers this value further to 199°C. It follows that effective microorganisms in liquid form have a very negative effect on the oil properties, so they should not be added to the new oil. The situation is different in the case of microorganisms in the form of ceramic tubes. The analysis of the graph shows that the addition of three pieces of ceramic tubes has no effect on the oil, because the flash point value is at the same level as for oil without the addition of microorganisms. A larger number of ceramic tubes, i.e. in this case six pieces, even slightly increases this point to the value of 231.5°C. The graphs in Fig. 8 for acid and base numbers also show that the effective microorganisms in the form of ceramic tubes do not increase the acid number and do not significantly reduce the base number of new oil. This confirms that the best choice will be to add effective microorganisms to the new oil, but only in the form of ceramic tubes.

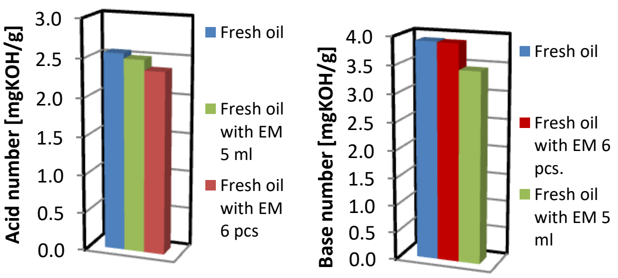

Fig. 8. Acid and base number of fresh oil and fresh oil with EM in liquid form and ceramics tubes

In Fig. 9 is shown the oil flash point for fresh oil and fresh oil with the addition of colloidal nanosilver and silver solution. Regardless of the type of silver and its quantity, very low flash point values were obtained, i.e. for colloidal nanosilver 2.5 ml and 5 ml – 200°C and 198°C, respectively, while for silver solution 2.5 ml and 5 ml – 207°C and 201°C compared to 213°C for oil without any additives. The highest value of the flash point can be observed for the silver solution of 2.5 ml, but this temperature level is still unacceptable due to the fact that oil vapors may ignite in such conditions when they come into contact with a flame. Larger amounts of additives result in even lower flash point values.

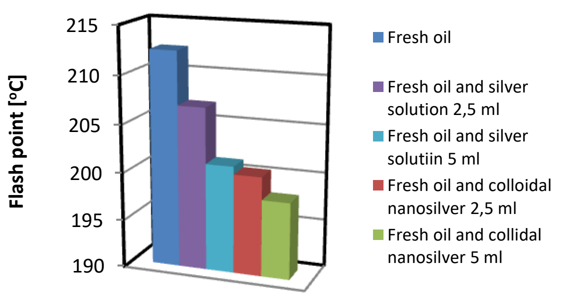

Fig. 9. Flash point oil of fresh oil and fresh oil with colloidal nanosilver and silver solution

The acid and base number graphs presented in Fig. 10 confirm the negative effect of such an addition to the oil, because the addition of silver, for example in the amount of 5 ml, increases the acid value and significantly reduces the base number of new oil. This phenomenon occurs regardless of the type of silver added. Basically, adding silver to new oil does not have any justification, because even before pouring it in the internal combustion engine, we have much worse properties than new oil, and the operation of engine oil in difficult conditions will only accelerate its decomposition.

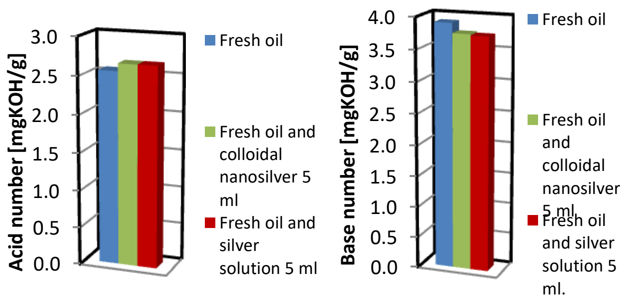

Fig. 10. Acid and base number of fresh oil and fresh oil with colloidal nanosilver and silver solution

Figure 11 shows the flash point for used oil without additive and comparison with used oil with the addition of effective microorganisms, the same as for fresh oil, i.e. in liquid form and in the form of ceramic tubes. In order to visualize, how much the flash point dropped for used oil, the results were compared with the value for fresh oil. The analysis of the graphs shows that, unlike for fresh oil, the best results are obtained for oil with the addition of microorganisms in a liquid form, because the flash point of used oil without any additives is 199°C (for fresh oil it is 213°C), while with the addition of effective microorganisms in the amount of 2.5 ml and 5 ml, respectively 203°C and 202°C, and for effective microorganisms in the form of ceramic tubes in the amount of 3 pcs and 6 pcs, respectively 197°C and 198°C. This means that the effective microorganisms in the form of ceramic tubes lower this flash point even more compared to the original value.

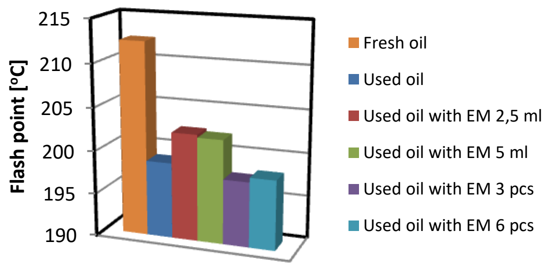

Fig. 11. Flash point oil of used oil and used oil with EM in liquid form and ceramic tubes

The acid and base numbers presented in Fig. 12 also confirm that the use of effective microorganisms in liquid form in the used oil gives better parameters, because effective microorganisms in the form of ceramic tubes increase the acid number much more, while reducing the base number. This is very disadvantageous for the components of the internal combustion engine.

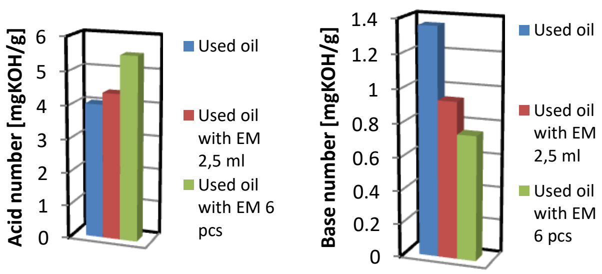

Fig. 12. Acid and base number of used oil and used oil with EM in liquid form and ceramic tubes

Graphs for used oil without additives and with silver additives as colloidal nanosilver and silver solution are shown in Fig. 13. Their analysis shows that without any additives the oil flash point is 199°C (for new oil it is 213°C) and the oil with the 5 ml silver solution addition, for which the flash point is almost 198°C, is the closest to this value.

Also for the amount of 5 ml, but this time for the colloidal nanosilver, this point is 194°C. The smaller amount of silver, i.e. 2.5 ml, significantly lowers the flash point to a temperature of 186°C for colloidal nanosilver and 191°C for silver solution. In general, the addition of silver does not improve the properties of the oil, so it makes no sense to add such compounds to the used oil. It follows that in this case both types of silver in this larger amount, i.e. 5 ml, have the least negative influence on the flash point.

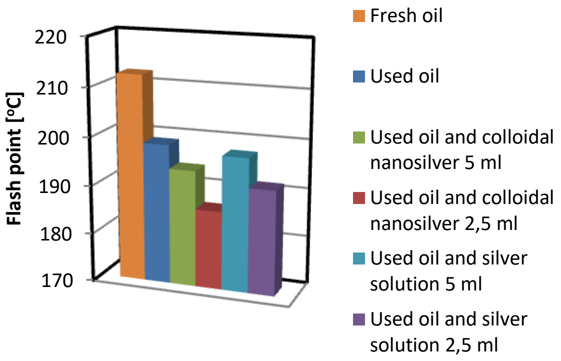

Fig. 13. Flash point oil of used oil and used oil with colloidal nanosilver and silversolution

The acid and base number graphs (Fig. 14) show that better values were obtained for colloidal nanosilver in the amount of 5 ml. This applies to both acid number and base number. On the other hand, the addition of the silver solution resulted in the highest value of the flash point, but also, unfortunately, a further increase in the acid number and a decrease in the base number. This makes this additive unsuitable for improving the properties of the oil, causing a counterproductive effect. In general, the addition of silver compounds does not have the beneficial effect of restoring the original properties, preferably those of the new oil.

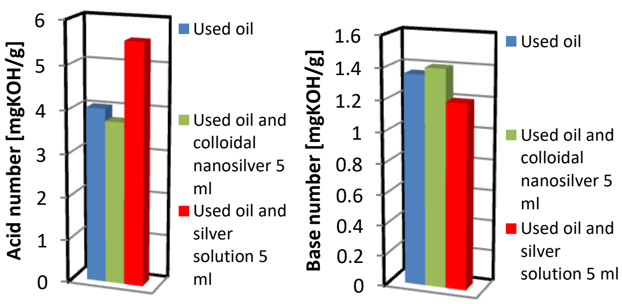

Fig. 14. Acid and base number of used oil and used oil with colloidal nanosilver and silver solution

Figure 2 shows the color of the samples, which shows that after adding microorganisms in a liquid form to the new oil, they became an oil-water emulsion and in this form are not suitable for use as a lubricating oil (there is probably some decomposition and release of water bound in the oil or a chemical reaction that resulted in the formation of such a large amount of water, which is related to the composition of the liquid additive of effective microorganisms).

The situation is different for the addition of microorganisms in the form of ceramic tubes, in which the microorganisms are bound and do not mix with the oil as in liquid form. It follows that only effective microorganisms are released into the oil, and due to the fact that they are not in liquid form, the oil has a clean and clear appearance. Silver solution and colloidal nanosilver were also added to the fresh oil in the amounts of 2.5 ml and 5 ml.

These photos in Fig. 3 show that additives caused the formation of a water-oil emulsion. In this form, the lubricating oil will not properly perform the tasks for which it was intended.

In used oil additives were added after using the oil. Previous research show that better parameters for used oil are obtained by adding EM in liquid form. The best additive for new oil are effective microorganisms in the form of ceramic tubes, and for used oil, the addition of effective microorganisms in the liquid form works best. As for silver, they adversely affect the parameters of both new and used oil.

6. Conclusions

The article presents research of flash points for new and used oil with the addition of effective microorganisms and silver solution. Additionally, the acid and base numbers for selected mixtures were presented in order to confirm the obtained results.

This work shows the variation in the value of the oil's flash point after adding to fresh and used oil effective microorganisms in liquid form and in the form of ceramic tubes. In addition, silver solution and colloidal nanosilver were added to fresh and used oil in the same proportions as for effective microorganisms. Each sample of pure oil and oil with additives were tested three times. However, the article presents the average result for each case.

Analyzing the results obtained, it can be seen, that for fresh oil the flash point is 213°C. On the other hand, adding of the effective microorganisms to the oil in the amount of 2.5 ml causes the flash point to be lowered to 200°C, while the greater amount of liquid additive, i.e. 5 ml, lowers this value further to 199°C. It follows that effective microorganisms in liquid form have a very negative effect on the oil properties, so they should not be added to the new oil. The situation is different in the case of microorganisms in the form of ceramic tubes. Three pieces of ceramic tubes has no effect on the oil, because the flash point value is at the same level as for oil without the addition of microorganisms. A larger number of ceramic tubes, i.e. in this case six pieces, even slightly increases this point to the value of 231.5°C.

The acid and base number charts also confirm that adding effective microorganisms to the new oil in the form of ceramic tubes is the best choice.

Regardless of the type of silver and its quantity, very low flash point values were obtained, i.e. for colloidal nanosilver 2.5 ml and 5 ml – 200°C and 198°C, respectively, while for silver solution 2.5 ml and 5 ml – 207°C and 201°C compared to 213°C for oil without any additives. The highest value of the flash point can be observed for the silver solution of 2.5 ml, but this temperature level is still unacceptable due to the fact that oil vapors may ignite in such conditions when they come into contact with a flame. Larger amounts of additives result in even lower flash point values. Basically, adding silver to new oil does not have any justification, because even before pouring it in the internal combustion engine, we have much worse properties than new oil, and the operation of engine oil in difficult conditions will only accelerate its decomposition.

The acid and base number diagrams only confirm the negative effect of such an oil additive, because the addition of silver increases the acid value and significantly lowers the base value of the new oil. This phenomenon occurs regardless of the type of silver added.

In order to visualize, how much the flash point dropped for used oil, the results were compared with the value for fresh oil. For fresh oil, the best results are obtained for oil with the addition of microorganisms in a liquid form, because the flash point of used oil without any additives is 199°C (for fresh oil it is 213°C), while with the addition of effective microorganisms in the amount of 2.5 ml and 5 ml, respectively 203°C and 202°C, and for effective microorganisms in the form of ceramic tubes in the amount of 3 pcs and 6 pcs, respectively 197°C and 198°C. This means that the effective microorganisms in the form of ceramic tubes lower this flash point even more compared to the original value.

The acid and base number presented in the graphs also confirm that when microorganisms are applied to used oil, better parameters are obtained for oil in the liquid form of this additive, because in the ceramics form they increase the acid number much more, while lowering the base number, which is very unfavorable for internal combustion engine components.

Then an analysis was made for used oil without additives and with silver additives as colloidal nanosilver and silver solution, where without any additives the oil flash point is 199°C (for new oil it is 213°C) and the oil with the 5 ml silver solution addition, for which the flash point is almost 198°C, is the closest to this value.

Also for the amount of 5 ml, but this time for the colloidal nanosilver, this point is 194°C. The smaller amount of silver, i.e. 2.5 ml, significantly lowers the flash point to a temperature of 186°C for colloidal nanosilver and 191°C for silver solution. In general, the addition of silver does not improve the properties of the oil, so it makes no sense to add such compounds to the used oil. It follows that in this case both types of silver in this larger amount, i.e. 5 ml, have the least negative influence on the flash point.

Nomenclature

ASTM	American Society for Testing and Materials
CO_2	carbon dioxide
EM	effective microorganisms
ISO	International Organization for Standardization
TBN	total base number

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