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The Interaction Mechanism of Fuel Lubricant Materials, Microorganisms and Anti-Microbial Additives

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ABSTRACT: A major problem in the oil refining industry is pollution of stored products, which in most cases lead to loss of the quality of the products. These contaminations also have biological aspects. As life finds a way in any point on Earth. Petroleum industry, as well, is not an exception. Due to many other issues with Internal combustion engines (ICE), the microbial problem is usually neglected. If microbial reproduction not kept under control, this can lead to damage to the quality, formation of sludge, deterioration of pipelines and storage tanks.
The study deals with microbial effect on fuel-lubricant materials (FLM). Formation and the growth of microorganisms, adsorption of microorganisms and contamination on metallic surface are considered. Influence to the physicochemical and exploitation properties. The prevention ways and positive/negative effects of using additives were discussed.

I. INTRODUCTION

The results of many years of research on the physicochemical and operational properties of fuel lubricant materials (FLM) during storage and use in the Central Asian region show that they undergo intensive biological damage by various microorganisms. This is due to the creation of more favorable conditions: pollution, water accumulation due to vapor condensation in storage tanks, fuel tanks, ICE crankcases at large temperature differences.

Expansion of the range of marketable oils and additives to them during the operation of machines and mechanisms sometimes leads to many problems. The variety of chemical additives is so wide that it would be difficult to determine which specific additives are incompatible with others. There are several well-known antagonistic combinations that should be avoided. This requires a cautious approach to the choosing and selection of FLM, particularly motor oil (MO) in each case. Research and experience in the operation of land vehicles (cars, agriculture and road-building machines, etc...) shows that when choosing the appropriate FLM it is also necessary to take into account the specific conditions of their operation [1].

First, favorable conditions for microorganism proliferation and their repercussions, as well as the effect of microorganisms on contact surfaces and phases of the biological damage process, were investigated. Then the types of additives and their purpose reviewed. Several methods (experiments) have been carried out to distinguish microorganisms from fuels and lubricants. In a hot, tropical and subtropical conditions, where the air dustiness and day-night temperature difference in moderately high [2], these materials (FLM) are more susceptible to changes in physicochemical properties due to the susceptibility of microorganisms. This leads to undesirable changes in their performance properties. The practice of microbiological studies [3-5] show that MOs operating under these conditions undergo microbiological damage much earlier, i.e., during their transportation, storage, when microorganisms begin to multiply intensively than during the operation of machines.

Studying (investigate) the susceptibility of MO immediately before use is necessary. Favorable conditions are created for the growth of microorganisms during the transportation of oils by sea or rail transport and their storage. The extensive number of microorganisms can lead to corrosion of ICE part [5-6]. Bio-corrosion is the process of corrosion of metal surface in conditions of influence of microorganisms. This type can be considered as an independent kind of corrosions as atmospheric corrosion, soil corrosions etc.

Initiation process of electrochemical corrosion of metal is often connected with the vital functions of bacteria and fungi accumulating in FLM. During metabolism, bacteria take up hydrogen and reduce sulfates. In the presence of oxygen, metabolic processes are intensified, the pH value of the aqueous medium decreases, which contributes to the corrosion of metals.[8]. Oxidizing products of iron, coming into reaction with hydrogen sulphide form insoluble iron sulphide in water. Settling on the surface of metal, particles of iron sulphide that are cathode with respect to steel, considerable divisions of surface of metal are covered, as a result formed comparatively small according to the area anode zones. As a result of this, there is a lot of local corrosion going on. The bio-corrosion process is separated into six steps.

TABLE 1. Stages of bio-corrosion process

Stages	Definition
Stage I	the transfer of microorganisms from airy, aqueous medium or from soil medium
Stage II	adsorption of microorganisms and contamination on metallic surface
Stage III	formation and the growth of microorganisms (the process is followed by the appearance of corrosive-active metabolic products and by local accumulation of electrolytes with redundant content of hydrogen ions H_3O+)
Stage IV	effect of products of metabolizes that is formed as a result of vital functions of microorganisms' colony (bio-corrosive - acidic, alkaline, oxidizing and ferment)
Stage V	stimulation of bio-corrosion process
Stage VI	synergism of bio-damages (bio-damages, ageing, corrosion wearing and fatigued effects)

Researchers are quite interested in the phases ranged from 3 to 6. Microorganisms can damage the surface of metal directly. As it was mentioned before, the bio-corrosive processes proceed under the influence of microorganisms and the stimulation of this process happens under favorable conditions. As practice showed bacterial corrosion can be under 6÷40 °C, pH = 1÷10.5 in the presence of organic and inorganic materials which are secondary products of synthesis of microorganisms [7]. The metals damage happens when various electrochemical concentrated elements formed on the metallic surfaces. Also, when products of corrosion formed in solution or on metallic surfaces, which are corrosive chemical compounds. Electrochemical potential medium changed in connection with the change of concentration of oxygen in solution. Even while low molecular organic acids produced by microorganisms might directly harm metallic surfaces, they frequently accelerate the corrosion process.

II. EXISTING ADDITIVES AND MECHANISMS OF THEIR INTERACTION WITH FLM

To maintain the stability of FLM's physicochemical and operational properties, as well as to provide them with new required attributes, numerous additives consisting of complex chemicals are added. Depending on the type of additive, FLM operating conditions, the functions performed, the additives are added in different concentrations - from hundredths to several percent [10]. Many research institutes are working on the synthesis of new, more effective additives [11]. Not all additives improve base properties once added to FLM. Additives improve, enhance some properties of only well-purified, high-quality FLM. The role of additives in recent years has grown so much that now FLM without additives is not being developed [12][13]. Additives added to FLM must meet certain requirements:

- have the greatest possible efficiency;
- do not precipitate during prolonged storage in a wide temperature range;
- do not linger on FLM and oil cleaning devices;
- does not dissolve in water;

- must not affect the properties of materials, power systems and engine lubrication;
- must be non-toxic to humans, etc.

Furthermore, they would not produce abnormalities (deteriorations) in the initial physicochemical characteristics when introduced to FLM. The mechanism of interaction of additives with FLM is very complex and until today not fully understood. However, numerous theoretical and experimental studies allow us to describe a fairly reliable picture of the interaction of additives with FLM. Additives can be divided into individual and multifunctional.

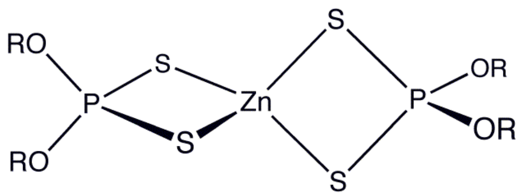
Viscous additives are designed to improve temperature properties or increase the viscosity index. Advantages of viscous additives: their resistance to oxidation and the fact that they almost do not affect the change in other physicochemical properties. Disadvantage: with the addition of certain additives, an increase in the acid number of FLM was observed. It is not advisable to increase the concentration, since FLM under severe operating conditions can be destroyed due to the decomposition of the polymer component of the additives, and this worsens the anti-wear properties. Viscous additives are added in a concentration of up to 3 ÷ 5% [13][14].

Antioxidant additives are designed to increase the stability of FLM to oxidation. The effectiveness of additives is significantly affected by the conditions in which FLM works, so the same additive is good for some operating conditions, and ineffective for others. Therefore, if we slow down the oxidation processes of FLM, we can provide for a longer period the required cleanliness of the working surfaces of ICE parts; for this purpose and apply antioxidant additives[15][16].

Anticorrosive additives are intended to reduce the chemical process of wear on friction surfaces. Corrosion inhibitors are added at a concentration of 0.05 ÷ 3.0 wt.% [17].

Anti-wear additives - designed to reduce the coefficient of friction, reduce wear and increase the strength of the oil film on the friction surfaces. Many zinc-containing organic compounds, such as zinc dialkyldithiophosphates, trialkylphosphate, dithiophosphate and others, as well as sulfur and chlorine-containing substances and esters, are used as anti-wear additives. All these compounds are surface-active substances (surfactants), when interacting with friction surfaces reduce the wear [11]. Added at a concentration of 0.06 ÷ 0.2%.

Additives with sulfur are characterized by the formation of a metal complex with an organic compound molecule, and during the operation of ICE, sulfur may be split off to form metal sulfides [18]. The formation of protective films can be schematically shown by the example of a chlorophosphorus-containing additive (ether trichloro-methyl-phosphinic acid):



(R = alkyl)

All these above-mentioned researches and additives do not deal with biological affection of FLM which has the same level of importance.

III. METHODOLOGY

In order to verify the negative effect of biomass on fuels and lubricating oils, several researches were carried out. First considered microbial influence on fuels. The microorganisms were bred in laboratory conditions with the samples taken from the tractor's fuel tank (summer grade diesel) during operation in hot climates. Cultivation of the microorganisms was carried out on a rocker, in Erlenmeyer flasks (500 ml) with 100 ml of the culture liquid for 4 days at different temperatures (28 and 45 °C) supplemented with summer grade diesel. The biomass accumulation was determined by the gravimetric method on membrane filters with pore sizes 3 and 5 microns, after being released from salts (5% hydrochloric acid HCl) and residual hydrocarbons (hexane - C_6H_{14}).

Next, three experiments were carried out to analyze changes in the basic properties of the diesel fuel (GOST 305-2013). Studies of the influence of bacteria Psevdomanas pyccyaneum (experiment 1), Mycobacterium acticolum (experiment 2) and Cladosporium fungus (experiment 3) showed that when the fuel is contaminated with microorganisms, the basic physicochemical and operational properties such as viscosity, acidity, resin content, etc. are subjected to more changes (Table 2).

TABLE 2. Changes in the physicochemical and operational properties of diesel fuel under the influence of bacteria and fungi.

Indicators	Control	Experiments		
		1	2	3
Kinematic viscosity at 20 °C mm/s (cSt)	4.70	5.40	5.12	4.91
Acid number, mg KOH/100 ml	5.0	6.0	5.7	5.5
Iodine number, g J/100 g	5.0	9.0	6.0	7.35
Coefficient of refraction	1.4704	1.4725	1.4728	1.4710
Resin content, mg/100 ml	130	296	210	154
The content of aromatic hydrocarbons, %	23	25.0	27.0	-

These microorganisms, mainly using the hydrocarbon composition of TFM, produce various acids. This leads to a sharp change (deterioration) in the basic physical, chemical and operational properties, which does not allow them to be used in the future for their intended purpose. To ensure the physicochemical and operational properties of diesel fuel stored for 3 months, and to protect it from damage by microorganisms, special studies were carried out. Studies were conducted without and with the addition of antimicrobial additives 8-oxyquinone and figon. The antimicrobial additives 8-oxyquinone and figon were added at a concentration of 0.05% and 0.005% respectively and the following results were obtained (Table 3).

TABLE 3. Changes in the properties of diesel fuel after 3 months of storage in metal barrels

Indicators	Control GOST 305-2013	after 3 months of storage		
		No Additive	+ 0.05 % 8-oxyquinone	+ 0.005 % figon
Kinematic viscosity at 20 °C mm/s (cSt)	4.09	8.20	4.15	4.04
Acid number, mg KOH/100 ml	0.94	15.03	0.55	0.88
Iodine number, g J/100 g	1.29	9.11	1.20	1.30
Resin content, mg/100 ml	22.0	24.2	18.1	20.4
Heat resistance, charge mg/100 ml	18.0	41.0	18.2	17.9

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From the results obtained, it is clearly seen the effective influence of the additive in ensuring the physicochemical and operational properties of diesel fuel during their storage for more than 3 months in ordinary metal barrels shows (without additives and with additives of 8-oxyquinone and figon). In the absence of additives in diesel fuel, an intensive micro-biological process is observed, which led to a significant deterioration in their physicochemical and operational properties [3].

Accidental ingress of microorganisms into diesel fuel will not cause significant damage if the fuel is consumed immediately. But the constant use of contaminated fuel, the accumulation in the fuel tanks and filters of water and biomass can lead to serious consequences. Likewise, similar research was carried out on motor oils (MO). The studies were conducted under laboratory conditions simulating tropical conditions, with a set of microorganism cultures isolated from MO samples during operation of machines in hot conditions. The samples were exposed for 14 days in a tropical thermal moisture chamber at a temperature of 35÷38 °C and a relative humidity of 95÷100%.

The object of the study was domestic motor oils of the brands: M-63/10V (M-63GI) (GOST 17479.1-2020), M-8V, M-8G2K (GOST 10541-78), M-10G2k and M-10V2 (GOST 8581-78), and foreign motor oils brand oils: Shell Rotella SX-40, Shell X-100 20W-50, Shell x-100 20W-40, Shell Spirax S3 AX 80w-90 (Shell Spirax EP 90-140), Shell N-100, Mobil oil HP-50.

Microorganisms were grown on a mineralized substrate (0.3% NaNO3; 0.1% KH2O4; 0.2% KCI; 0.05% $MgSO_4$; 3% hungry agar and tap water up to 1 liter). The study of the susceptibility of motor oil was carried out in Petri dishes using the well method using a coagulation loop (needle) previously sterilized by calcination in a burner flame, then the loop was cooled. A small number of culture cells were carefully scraped with a chilled loop and introduced into the test samples of oils. All these operations were carried out directly in the vicinity of the burner to prevent foreign microorganisms from entering the environment. The growth of test cultures of microorganisms was evaluated visually on a 5-point scale according to the size of the zone of damage of microorganisms around the holes on the surface of the substrate every 4 days.

Control experiments were performed in a separate Petri dish, without infection by microorganisms. Next, the exposure of the cultures was carried out in a thermostat at a temperature of 35÷38 °C and a relative humidity of 95÷100%.

The study was carried out with the following microorganisms: Mucor, Penicillium, Alternaria, Micrococcus, Diplococcus, Bacterium, Bacillus.

To improve the reliability of the results were performed comparative studies the growth and accumulation of microorganisms in the engine oil with cultures highlighted during operational tests. Studying the resistance of motor oils to microorganism damage rated on a five-point scale, the following results were obtained:

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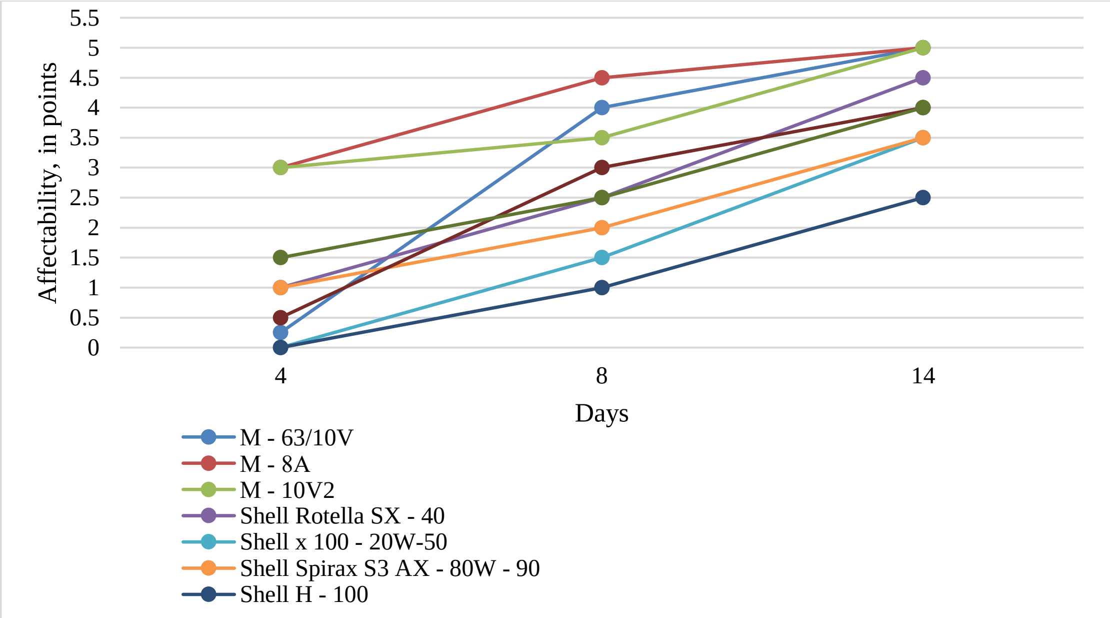

FIGURE 1. The degree of susceptibility of MO to microorganisms over time

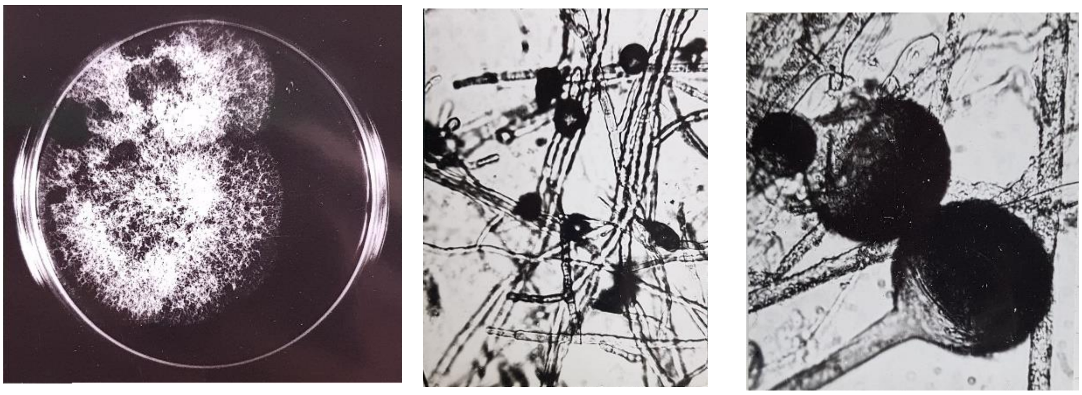

FIGURE 2. Colony of microorganisms and cells Mucor and Alternaria detected in MO during the operation of ICE (x500 times)

IV. RESULTS OF STUDIES OF THE SUSCEPTIBILITY OF FLM BY MICROORGANISMS AND THEIR ANALYSIS

From the result of observations FIG. 1 and FIG. 2, it was found that after 4 days the difference between the control samples (not infected with microorganisms) and experimental (MO + microorganisms) was noticeable. In the Petri dish, after 8 days, the surface of the samples of engine oils M-63/10V, M-8A, M-10V2, Shell Rotella SX-40, Shell x 100-20W-50 were almost covered by microbes. After 14 days of observation, all tested oil samples were completely affected by bacteria and fungi (FIG. 2).

According to the methodology for studying the growth characteristics of bacterial cultures (microorganisms), depending on the temperature and concentration of summer grade diesel fuel samples in the mineral medium, the following results were obtained:

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- biomass content (g/l) in the mineral medium with diesel fuel DL: culture - Ps. fluorescens at 28 °C - 3.9 and 45 °C - 5.0;
- accumulation of biomass (g/l) in a mineral medium with different concentrations of summer grade diesel fuel: culture - Ps. fluorescens at 2% - 2.8; 10% - 4.1 and at 20% - 5.9.

At a temperature of 28 °C it is still difficult to determine the culture, and at 45 °C colonies of microorganisms in the form of a "pearl" are already clearly visible. From the results of laboratory studies, it can be seen that the greatest accumulation of biomass (up to 5 g/l dry biomass) was noted on a medium with diesel at a temperature of 45 °C (5.0 g/l) and a concentration of 20% diesel fuel (5.9 g/l).

The input type design is defacto the link between the respective information kind system and the respective user. It herein comprises of the developing the specification and those of modus operandi basically for the data in preparation and those chosen steps which are being necessary to put in transaction of the respective data into a usable type form basically for processing and can be defacto achieved basically by examining the considered computer primarily to read the respective data from the written or the printed type document which it can occur by having those of people premeditating or keying the respective data directly into the corresponding system. The whole of the design of the respective input herein focuses on restraining the required amount of input which is essential, administering of those of errors, prohibiting in delay and also preventing those of extra kind steps and keeping the whole of the process very in-complex. The respective input is defacto designed in such a manner that it defacto provides or go forth with the security and making to ease the utilisation by retaining the privacy. Input type design which is premeditated the following types can be known herein with reading.

V. DISCUSSION AND CONCLUSION

According to the results of the research, motor oils which for 14 days they had significant resistance to microorganisms, can be considered the most resistant to microorganism damage. But after 30 days also turned out to be affected. The obtained results suggest that motor oils containing a large amount of aromatic hydrocarbons will not allow intense damage by microorganisms. And an increase in the group composition of oil of naphthenic-paraffin compounds of hydrocarbons, which serve as the main substrate for the nutrition (vital activity) of microorganisms, allows us to assume that it reduces the time of resistance of this brand of MO against microorganism damage. Therefore, to maintain the operational properties of MO in hot climates, the most promising are MO with a lower content of naphthenic-paraffin compounds. MOs with a large number of paraffin compounds can be used in hot climates only with antimicrobial additives that protect them from microbiological effects.

Thus, from the studies carried out can be seen that the use of additives in permissible concentrations will increase protective characteristics against susceptibility to damage by microorganisms. It is recommended to add the additive before the population of microorganisms, at the beginning of use.

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