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Methodically organizatonal principles of biologial stability providing of aviation fuels

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Виконано дослідження здатності авіаційних палив до біоураження, проаналізовано механізм деструкції вуглеводнів авіаційних палив та наслідки цього процесу. Досліджено методи визначення наявності біологічної фази авіаційних палив. Вивчено ефективність основних методів забезпечення біологічної стабільності авіаційних палив. Визначено методично-організаційні засади забезпечення біологічної стабільності авіаційних палив.

Выполнены исследования способности авиационных топлив к биопоражению, проанализированы механизм деструкции углеводородов авиационных топлив и последствия этого процесса. Исследованы методы определения наличия биологической фазы авиационных топлив. Изучена эффективность основных методов обеспечения биологической стабильности авиационных топлив. Определены методично-организационные основы обеспечения биологической стабильности авиационных топлив.

The research of avitation fuels ability of biocontamination is performed, the mechanism of aviation fuels hydrocarbons destruction and consequences of this process is analysed. Determination methods of aviation fuels biological phase presence were researched. Efficiency of basic methods of biological stability providing of aviation fuels is studied. Methodically organizational principles of aviation fuels biological stability providing were determined.

Introduction

Property of microorganisms to metabolize hydrocarbons of solid, liquid and gaseous petroleum products was known in the early XX century. This phenomenon has become a cause of substantial problems in the field of oil producing, oil refining and petro chemistry, especially during exploitation of oil products [1–6].

From the one side, the change of oil and oil products properties under the influence of microorganisms finds application for the special aims (waste waters cleaning of oil-processing plants, cleaning of territories and aquatoriums from contamination by oil products). The other side, activity of microorganisms results destruction of oil products and the damage of materials and constructions that contact with them.

Therefore protecting of fuel lubricating materials from microbiological contamination is a very important problem. In a sphere of aviation fuel providing, development of microorganisms in fuels results deterioration of physical, chemical and operating properties because of their hydrocarbon composition change, accumulation of microbal mucus and sediment and formation of resistant emulsions. Clogging of aircraft filters and fuel pipes system by microbal mass leads to the aviation incidents and accidents [1–6].

Problem setting

Goal of the research is creation of methodically organizational principles of aviation fuels biological stability providing.

Object of research – biological contamination of aviation fuels and mechanism of hydrocarbons destruction.

Subject – methods of determination of microbiological contamination presence in aviation fuels and methods of its biological stability providing.

Based on actuality of this problem, the following tasks are selected for implementation of research:

1. The research of aviation fuels ability to biocontamination.
2. The research of aviation fuels hydrocarbons destruction mechanism and consequences of this process.
3. The research of methods that determine presence of biological contamination in aviation fuels.
4. The research and efficiency analysis of major methods of aviation fuels biological stability proving.

Problem solving

During the creation of jet aviation in the USA, began active study of questions connected with microorganisms' development in oil fuels. The work on this question in our country mainly was to determine fuels biostability in laboratory conditions. Purposeful researches of fuels biostability in exploitation conditions were not conducted practically.

There were not the generally accepted methods of fuels biocontamination estimation to this time. For these purpose the well-known microbiological methods were used by which the presence of microorganisms in fuels, its quantitative content and specific composition were determined [3].

Because of absence of correct technological discipline the presence of fuel biodestructors is observed on the bottom of aviation fuels storage reservoirs, in the tanks of aircrafts, in deposits on filters [3].

Aviation fuels undergo biodamages during storage, transporting and exploitation. Especially unsteady to the biodamages fuels which are consumed by jet aviation [1, 4].

Significant factors that assist to active development of microorganisms are pH environments, presence of such elements as carbon, phosphorus, potassium, nitrogen, sulphur, iron, sun energy. There is also important an ambient temperature, so cells of microorganisms actively propagate oneself when the temperatures are 25–35 °C, although can grow when the temperatures vary from plus 5 to 45 °C. It is well-proven that the spores of many types of microorganisms remain viable during a few hours when the temperatures start from minus 40 °C [5].

There is also a necessary condition for development of microorganisms - presence of water and nutritives in a fuel [4]. The growth and development of microorganisms is stopped in the water-free fuel. However in the real exploitation conditions and fuels storage it is impossible fully get rid of moisture, and presence in fuel at least 0,01–0,02 % water and its tracks at the proper temperature is enough to begin growth of microorganisms. Today it is known [6] several sources of water ingress:

- atmospheric moisture from the air;
- rain or snow may fall into the tank through the holes for sampling, ventilation valves or untightly fitting lid;
- transportation or storage in tankers and on the boards can cause penetration of ballast water;
- water from all listed sources accumulated in the bottom of the tank, forming a water layer.

Microorganisms can penetrate to the fuel through air or water. Thus, during the water layer formation the colonies of microorganisms is developing. Liquid hydrocarbon fuel is an excellent source of nutrients for many types of present microorganisms. The result is a population "explosion": microorganisms spread at the surface of fuel and water, begin to live in the water phase, continuing to eat fuel [7].

Today it is known 200 species of microorganisms, including 30 families that can use hydrocarbons as sole source of carbon and energy. These include bacteria, yeast and fungi. The most complete issue on destruction of hydrocarbons by microorganisms is reflected in works [1–6].

The main microorganisms, that cause biocontamination of fuels, are the next bacteria's of family *Pseudomonas*, *Micrococcus*, *Mycobacterium*, family of fungi such as *C1adosporium*, *Aspergillus*, *Penicillum*, *A1ternaria* and others, while in aviation fuels more often than in other petroleum products are bacteria *Ps.aerugenosa* and fungi *C1adosporium Resinae* («kerosene fungus») [1, 5]. The latest researches determined two more active bio destructors of aviation fuels *Hormoconis resinae* and *Monascus floridanbs* [7].

Microbial contamination such as *Cladosporium Resinae* consists of fibers that reach considerable length and form convoluted layer. Fungi reproduce by spores that may be in dormant condition long enough, waiting for growth favorable conditions. Fuel is often contaminated with microscopic fungi during transportation, storage, preparation and delivery, as well as in aircraft fuel tanks. Spores can remain undetected for considerable period of time because of mentioned above. Only in the case of favorable environment to their development, the spores germinate; fungi multiply and contaminate fuel [8].

It is proved that biocontamination of fuel is connected to microbiological enzymatic oxidation of hydrocarbons with formation of organic acids that have surface active properties [8]. The speed and depth of the microbial oxidation of aviation fuel depend on their carbohydrate composition. Hydrocarbons with a linear structure of the molecules are destroyed faster than their branched isomers. Aliphatic hydrocarbons (paraffin's) are less biostable than aromatic. Therefore, fuels that contain mostly paraffin hydrocarbons can be destroyed by microorganisms faster than those containing more aromatic compounds [8].

The processes of microbial oxidation of hydrocarbons are very complex, because the processes of biogenic oxidation have an influence of many factors: moisture, environment acidity (pH), temperature, osmotic pressure, and so on. In addition to these factors are important physiological characteristics of most microorganisms that occur during the oxidation of individual hydrocarbons and their mixtures [7, 8].

Microorganisms have the selective ability related to various hydrocarbons, and this ability is determined not only by the difference in the structure of substance, and even the number of carbon atoms that are the part of their structure.

Hydrophobic of hydrocarbon molecules is important for the chemistry of microbial oxidation of these compounds, their transport in the microbial cell and dynamics of reproduction and physiology of bio destructors.

The first stable products of hydrocarbons oxidation are the primary alcohols. The next is usual biological conversion of alcohols to aldehydes and aldehyde to acid. The general scheme of reactions [7]:

$$R\text{-}CH_2\text{-}CH_3+[O] \rightarrow R\text{-}CH_2\text{-}CH_2OH\text{-}2H \rightarrow$$
$$\rightarrow R\text{-}CH_2\text{-}CHO\text{-}2H+HOH \rightarrow R\text{-}CH_2\text{-}COOH.$$

Reduced paraffin fuel capacity by biochemical oxidation occurs due to removal of model systems of n-alkanes as substances which mainly consume microorganisms.

From the physiological characteristics of each kind of microorganism depends orientation process of individual hydrocarbons destruction and their mixtures that have different degrees of resistance to oxidation.

Research of the microorganisms' ability to oxidize specific classes of hydrocarbons within the aviation fuels, allows in perspective to create biologics for specific purposes.

After the damage of fuel by microorganisms in the presence of the mentioned above favorable conditions the next consequences are observed [1–7, 9]:

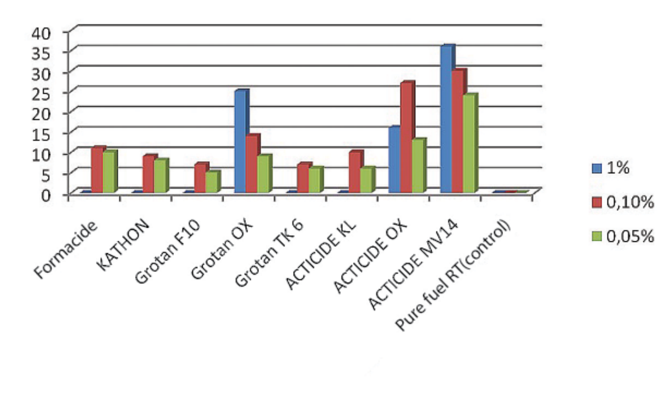
- *change in physical and chemical properties of fuels*, namely increasing of major physical and chemical parameters values as kinematic viscosity, refractive index, pH, content of actual resins and others. Also characteristic features are the formation of sediment, turbidity fuel and peculiar odor;

- *corrosion of storage tanks for aviation fuels*. Corrosion development of bottom part where accumulates water sludge, especially on verge of system distribution «fuel-water», corrosive damage of aircraft tanks, corrosion of aircraft power constructions;

- *clogging and damage of fuel filters, pumps and fuel systems*. Sedimentation of mycelium and bacteria colonies at the inner walls of the fuel systems leads to clogging of pipelines, filters, pumps and fuel systems;

- *threat to the safety of aircrafts flights*. Changing the physical, chemical and exploitation properties of aviation fuels leads to early clogging of filters, pollution of regulating equipment, causing unstable operation of the fuel system, and therefore can cause failure of the engine, and even complete failure of the system, and as a consequences – appearance of accidents and emergency landings. [3]

Methods for detection of microbiological contamination of fuels are divided into long-term and express methods [2]. The long-term methods include seeding of microorganisms in nutritive environment followed by microscopic analysis of cultivated cultures. Express methods used in airport. They are based on indication of microorganisms by chemical compounds. One of these methods is determining micro-



Comparative distribution of research results of fuels biological stability, protected by biocide additives by diffusion zone method

bial contamination of fuels for jet engines with a solution of ninhydrin. Ninhydrin - organic compound belonging to the classes of ketones, alcohols and condensed carbocycles used as qualitative and quantitative reagent in the determination of primary amines and amino acids.

In this area there are patented detection techniques of bio contamination in aviation fuels with using two sets Microb-Monitor 2, Hum Bug Detector, Bug Alert, Bug Check, electronic meter HMB IV.

For example, when using MicrobMonitor 2 test results are available within three days and do not require further interpretation [9].

Exploitation practice shows that in areas where the risk of getting fuel contamination are higher, the frequency of checking for microbiological contamination presence should be at least once a month.

Methods for preventing microbiological contamination of aviation fuels are divided into active and passive [1–4].

Passive methods include the range of activities related to plants of aviation fuels providing, that can reduce fuels biocontamination.

Active methods include adding to fuel biocides – antimicrobial additives.

Exploitation protective methods are the following:

- proper fuels storage conditions;
- regular drying and removing of water (sludge) from the tanks bottom, filters, fuel tanks, aircraft tanks;
- avoiding of contact with water and atmospheric moisture, reducing contact with air, especially humid;
- timely cleaning of technological equipment of fuels storage;
- filtration.

There are many ways to prevent biological contamination of fuels. One of such method is the method of ultraviolet and electromagnetic radiation. Ultraviolet radiation causes the death of microorganisms. For this purpose the UV lamp was developed. During its development excluded the possibility of explosion and inflammation of fuels. The lamp can be mounted to the bottom of the fuel tank and move along it, as well as along the fuel line.

Possible installation of lamps during pumping fuel from one tank to another. Destruction of microorganisms is also possible by using electromagnetic radiation at a certain frequency radio waves [4]. Colonies of fungi and bacteria can be removed by filtration through a porous material, the pore size of which is not more than 2 microns. Possible way to protect the fuel through bacterial filters, filled with silver compounds – cotton, glass, synthetic rubber.

To physical and mechanical methods of microbiological contamination control are also include centrifugation followed by agglomeration filtration, flotation, the use of ion-exchange resins, electro hydraulic deposition, ultrasonic control [4].

The most effective way to protect the fuel from biological contamination at present is biocide additives that reduce activity of microorganisms in jet fuels and prevent biological corrosion of fuel tanks [1, 5].

During the choosing of biocide additives there are the following requirements: they must not impair quality of fuels, characterized by prolonged action, detrimental effect on engine structural parts, fuel regulatory apparatus, reliability of filters and filter separators, to be toxic. Combustion products of these substances should not cause adverse effects on the environment [4].

Biocide additives may be soluble in fuels, and water cushion and destroy microorganisms in both phases [4, 5].

Many biocide products have been tested abroad that meet the above requirements, there are the following: ethyleneglycol monometyl ether and Biofora F [4].

Ethyleneglycol monometyl ether – is anti water crystallization additive, with glycerol. However, it was found that glycerol actively contributes to the microorganisms, and without it ethyleneglycol monometyl ether reduces their growth. In addition to the fuel for air jet engines – 0,1-0,15 % by weight, substance concentrates in water up to 20%, which not only prevents the formation of ice crystals, but also reproduction of microorganisms.

Biofor F after the penetration to oil product is concentrated in the free water. The mechanism of this substance action is also based on increasing of osmotic pressure. The effectiveness of the substance is in its lower concentrations in the water. This additive has the following drawback: when added to jet fuel is deposited on the blades of aircraft turbines and can cause them to corrosion due to increased acidity of water.

Long-term monitoring of fuel tanks coated with furan resins showed that microorganisms in these tanks is reduced [4].

There is well-known antiwater crystallization liquid «I-M», which is a product of association ethyl cellosolve and methanol. Liquid «I-M» is designated for use as additives to the fuel for the air jet engines, refueled aircrafts of civil aviation to decrease the probability of icing aircrafts and helicopters filters at low temperatures. We researched bactericidal properties of the additive that caused by containing of methanol [10].

There are used biocides that have the active components – cellosolve, compounds of nickel, copper and other metals, heterocyclic compounds in quantities 0,0001-0,005% [7].

Due to increasing the range of biocide additives, there were studied bactericidal activity of such compounds dimethyl-dialkil-ammonium chloride ($[R_2(CH_3)_2N]Cl$) and dimethyl-alkyl-benzyl-ammonium chloride ($[R(CH_3)_2NC_6H_5–CH_2]Cl$) for aviation fuels - gasoline and fuel TS-1 for air jet engines [8].

During the study of these compounds has been established [8] that the amount of 0.05% or more above mentioned additives reduce the growth of all microorganisms in the aviation gasoline and fuel TS-1.

It was studied biocide activity of such compounds: zinc salts of synthetic fatty acids, mixed salts of zinc and mercury, acetic and oleic acids. With addition to jet fuel in concentrations of 0,05–0,1 %, they found sufficient activity, reducing the number of microorganisms on 75–85 %. The salts of higher carboxylic acids of chrome, copper and lead, and also naphthenate of iron, copper and chromium were low-toxic [3–5, 11].

Taking into account problem actuality of protection from both fuels accumulation of static electricity, and from microbiological contamination, was obtained complex additive that has antibacterial and anti-static properties. Mixtures of bactericidal and anti-static additives of different composition were studied; both bactericidal components applicated dimethyl-dialkil-ammonium chloride [8]. Simultaneously, this additive is an effective anti-static additive in concentration of 0,003%, increases conductivity and reduces oil electrification during their motion [8].

It is set that the antiwater-crystallization additive PFA-55MB has high bactericidal effect for jet engines. Addition to jet fuel in an amount of 0,05–0,15 % of PFA-55MB additive practically fully prevents development of microorganisms and corrosion of fuel tanks of jet engines. This additive is the most widespread abroad [9].

It was found that 8-hydroxyquinoline and disalicildenpropandiamin in addition to fuel for air jet engines brand TS-1 in concentration 0,2 and 0,1 % diminished growth of microorganisms accordingly on 88 and 75 %. Primary amines of C_{12}–C_{15}, which was added to the fuel in an amount of 1%, diminished growth of microorganisms on 95 %.

Special experiments [1, 2] reflected that active biocide additives in the water-fuels systems there can be substances that do not dissolve in fuel, but soluble in water. Thus, the complete destruction of microorganisms in the environment in fuel TS-1 was observed when injected into the water phase one of the following substances: 0,04% 1,2-diaminopropana or hexamethyldiamin, 0,12 % ethylendiamin, hydroxylamine of hydrochloric acid or methylamine tartrate, 0,16 % trimethylamine or n-butylamine.

Growth of microorganisms reducing on 98% is observed when the content in the water phase 0,08 % n-butylamine, etylendyamina, hydroxylamine hydrochloride or methylamine oxalic acid.

Inhibition of microorganisms increasing by 70, 75 and 90 % was observed in environment of fuel TS-1 when in the water phase added respectively 0,24 % chromium acetate, 0,16 % chromium nitrate, 0,16 % copper acetate [9, 10].

There is also known multifunctional additive IPOD (isopropyloktadetsylamin).

Bacteria fungicidity of additive on the base of gas condensates was studied. Unlike the other additives, it obtained from hydrocarbon fractions (145–280) °C of gas condensates. Adding of the additive in amount of 0,1% destroyed microorganisms within 10–15 days on 100 % [5].

Synthesized additive has not only antibacterial, but also antioxidant and anti-corrosion properties. The additive addition to final concentration of 0,1 % prevents sediments in fuel on 80 % [5].

Katon FP 1.5 of the company ROHM AND HAAS (U.S.A.) is one of the highly effective biocides that used worldwide for various fuels. In the nomenclature of the International Union of Theoretical and Applied Chemistry, an active component of Katon FP 1.5 is defined as 5-chloro-2-methyl-4-isotyazolin-3-one.

Today many foreign companies are producing biocide additives to petroleum products, such as: «Bang and Bonsomer», «THOR», «ROHM AND HAAS» and others [3].

The authors conducted research on the efficiency of modern biocide additives (applications) of mentioned above foreign manufacturers. The research was conducted by the method of diffusion zone, which is testing the microbiological stability of jet fuel protected by antimicrobial additives with different concentrations in the Petri dish on nutrient dry agar for cultivation of microorganisms. Zones diameter of growth absence characterized the degree of test fuel stability.

It was used a mixture of aerobic bacteria (Pseudomonas, Bacterium, Mycobacterium) as a test cultures, allocated from the affected oil.

Table

Results of the experiment by the method of zonal diffusion

Additive name	Zone diameter, mm		
	Additive concentration in fuel RT		
	1 %	0,1 %	0,05 %
Formacide	0	11	10
KATHON	0	9	8
Grotan F10	0	7	5
Grotan OX	25	14	9
Grotan TK 6	0	7	6
ACTICIDE KL	0	10	6
ACTICIDE OX	16	27	13
ACTICIDE MV14	36	30	24
Pure fuel RT(control)	0	0	0

The research results of biological stability of aviation fuel RT, protected by biocide additives with the method of diffusion zone are shown in Table.

So, our diagram represents that the best antimicrobial properties has the following additives: GROTAN OX, AKTICIDE OX, AKTICIDE MV14.

Conclusions

Analysis of the aviation fuels ability to bio contamination and studying the mechanism of hydrocarbons degradation showed that, along with hydration and fuel pollution by mechanical impurities occurs microbiological contamination that affects not only fuels quality, but also on the exploitation reliability of the equipment.

Research methods for determining the presence of biological contamination in aviation fuel has shown that the appearance and development of biocoenosis in fuels lead to deterioration of their physical, chemical and exploitation properties due to changes in their hydrocarbon composition, accumulation of microbial slime and sludge formation of stable emulsions. The best method of microorganisms detecting in operational of airfield is to use indicator express methods.

Among the variety of protection methods of microorganisms was found that the most effective method of protecting aviation fuels from microbiological contamination is the use of antimicrobial (biocide) additives.

International practice of biocide protection from microorganisms in aviation fuel is efficient enough, but it does not apply in the countries of CIS because of the high cost of reagents and absence of recommendations for their use in the regulatory framework.

Scientific interest is the development of express methods that determine the microbiological contamination presence in airfield operational conditions and domestic biocide additive that will substantially reduce the degree of microbial destruction of aviation fuels.

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ПРОФЕСІОНАЛИ ГАЛУЗІ

В.І. Стьопкіну – 90

14 січня 2013 року виповнилося 90 років відомому спеціалісту галузі Василю Івановичу Стьопкіну.

Народився він 1923 року в м. Георгіївську Ставропольського краю (Росія). У 1940 р. вступив на промисловий факультет Грозненського нафтового інституту. У 1941–1945 рр. перебував у діючій армії, закінчив війну в званні старшого лейтенанта. У боях під Феодосією отримав тяжке поранення, довго лікувався. Після демобілізації продовжив навчання в інституті, який закінчив у 1950 р.

Почав працювати в Монголії, пройшовши шлях від майстра до головного інженера контори буріння. З 1954 р. працював начальником виробничо-технічного відділу Надвірнянської КБ, а через три роки його призначили головним інженером Долинської КБ НПУ «Долинанафта». У 1960–1963 рр. обіймав посаду головного інженера тресту «Прикарпатбурнафта».

За безпосередньої участі Василя Івановича в бурових підприємствах Прикарпаття уперше почали вести одночасне буріння двох свердловин із одного бурового верстата на Долинському родовищі, застосовувати алмазні долота, запроваджували системи механізації бурових робіт та інші інноваційні рішення.

У 1964–1969 рр. він був заступником керівника контракту радянських фахівців із розвідки нафти і газу в Німеччині. Під його керівництвом успішно велися бурові роботи, відкрито нові газові родовища, на одному з них, зокрема, оперативно ліквідовано відкритий газовий фонтан.

Після повернення з відрядження В.І. Стьопкін працював начальником відділу випробування свердловин, згодом технічного відділу Головнафтогазрозвідки Міністерства геології України. У 1972 р. його призначили заступником Міністра геології, відповідального за буріння свердловин. На цій посаді він працював до виходу на пенсію в 1984 р.

У цей період підприємства Міністерства геології щорічно бурили 500–600 тис. м свердловин, відкривали нові нафтові і газові родовища. Оскільки будівництво розвідувальних свердловин велося в складних геологічних умовах, зокрема в умовах аномально високих тисків, Василь Іванович велику увагу приділяв удосконаленню техніки і технології буріння, якості промивальних рідин, профілактиці аварійності і, зокрема, відкритих газових фонтанів. Завдяки використанню на великих глибинах турбінного буріння, у тому числі високомоментних турбобурів, нових конструкцій доліт, а також переходу на буріння свердловин зменшеного діаметра, вдалося істотно підвищити техніко-економічні показники геологорозвідувальних робіт.

Він у незмінному брезентовому плащі і кирзових чоботях був майже на кожному фонтані чи проявленні, поспішаючи туди прямо з потягу, і «місив болото» на буровій нарівні з усіма. Під його опікою в Україні виросла ціла плеяда висококваліфікованих технологів-керівників бурових робіт: Б.О. Бялюк, О.О. Волошин, С.М. Гінда, Б.І. Голодько, М.Й. Лисий, Б.М. Москаленко, В.С. Овчаренко, Р.М. Сенів, В.М. Стефанишин.

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Сьогодні В.І.Стьопкін, жваво перебігаючи клавішами комп'ютера, за мить знаходить історію будь-якого фонтану чи іншої знакової події.

Бажаємо ювіляру доброго здоров'я, благополуччя та довгих років життя.

Колеги по роботі, редакція журналу