# Article

## **Open Access**

Modern Trends in The Use of Additives in Fuel and Oil Materials (Overview)

Oleksandr Trotsenko<sup>1</sup>, Andrey Grigorov<sup>1</sup>, Valerii Nazarov<sup>1</sup>, Mikhail Nahliuk<sup>2</sup>

<sup>1</sup> National Technical University «Kharkov Polytechnic Institute», 61002, 2 Kirpichova str., Kharkov, Ukraine

<sup>2</sup> Kharkiv National Automobile and Highway University, 61002, 25 Yaroslava Mudrogo str,

Kharkov,Ukraine

Received November 17, 2021; Accepted March 21, 2022

#### Abstract

Domestic and foreign literature data were reviewed on the conditions and features of additives use, their required content in fuel and oil materials, and the study of their characteristics in order to systematize data on additives used to improve the operational properties of fuel and oil materials. The use of additives in the composition of fuel and oil materials can significantly increase the level of their operational properties, without serious production costs associated with deep cleaning and preliminary preparation of raw products, compounding of raw products, technical re-equipment of production, etc. A list of additives was offered to fuel and oil materials used in the world practice of their production and application, added with dyes. These additives should be included in the main package of production branded premium fuel and oil materials, create their classification, simplify the procedure for identifying different batches, simplify the procedure for transportation, storage and distribution of fuel and oil materials. At the same time, among all the variety of dyes that are currently used for coloring to fuel and oil materials, the most appropriate is to use those that carry out multifunctional properties. These properties, depending on the type of materials, along with the color, can be density, detonation resistance, anti-corrosion. This approach, on one hand, will allow to balance the amount and properties of additives included in the overall package, on the other hand - will reduce production cost of the fuel and oil materials.

**Keywords**: Additives; Dye; Multifunctional properties; Fuel and oil materials; Identification; Classification; Detonation resistance; Density.

### 1. Introduction

It becomes problematic to ensure the modern level of operational requirements put forward by the regulatory and technical documentation for the quality of petroleum products, today, using modern hydrocarbon raw materials and operating schemes for its processing at oil refineries (refineries) in Ukraine. This is primarily due to the lack of high-quality hydrocarbon raw materials in Ukraine and the gradual wear and obsolescence of the refinery's technological equipment. The solution in this case is to use the additives, special components in the composition of petroleum products, that can improve the quality of commercial petroleum products.

### 2. Research objective

Research objectives on many years of world practical experience in the production of petroleum products, it should be noted that it is possible to improve their quality level to the level required by regulatory technical documentation using various technological processes presented in the form of a structural flowchart in Figure 1.

Analyzing the ways improving the quality of petroleum products presented in Pic.1, it should be noted that the use of additives in the composition of petroleum products is one of the most effective and least expensive ways to improve the quality. Thus, additives can be used both in the production of petroleum products at refineries, and in areas of their direct application. The global chemical industry produce them in significant quantities, able to meet the existing demand, the use of additives allows to adjust certain properties of petroleum products without affecting others, the cost of purchasing and using additives is significantly lower than for other technological solutions (for example, Technical re-equipment of production or purification of raw materials).



Figure 1. Structural flowchart for improving the quality of petroleum products

The above-mentioned advantages of using additives in petroleum products contribute the constant expansion of their nomenclature (more and more substances and their compositions are used as additives) and an increase in their production volumes. At the same time, the use of certain additives, especially for fuels, in recent years has either been banned (for example, N-Methylaniline), or restricted in use (for example, Methyl-tret-butyl ether), which is associated with their harmful effects on the environment and the human <sup>[1-2]</sup>. In view of this, information about the use of additives in petroleum products, which is now found in the world technical literature, requires a certain systematization.

### 3. Results and discussions

Depending on the group of petroleum products where additives are used, they are divided into two main groups: fuel additives (gasoline, diesel and boiler fuel) and additives for lubricants (oils and plastic lubricants). According to their functional properties, fuel additives are divided into main groups.

**1) Antiknock agents**. These additives are used in gasolines and increase resistance to detonation, described by octane number (ON). At the same time, it improves the combustion process of gasoline, reduce the consumption and increase the reliability of the internal combustion engine (ICE). The operation principle of antiknock agents is to prevent explosive decomposition of fuel oxidation products, occurred before the start of normal combustion of the fuel mixture. High temperature develops during compression in combustor, hydrocarbons begin to oxidize and form a large amount of peroxides. Being chemically unstable, peroxides decompose with an explosion. Antiknock agents destroy peroxides and prevent from accumulation <sup>[3]</sup>. According to the active substance, antiknock agents are placed on the base: lead compounds (currently not produced); amines; ferrocene (iron) compounds; manganese compounds; alkali metal compounds. Also, oxygenates and mixed compositions of aromatic hydrocarbons are distinguished <sup>[4]</sup>.

**Oxygenates** are oxygen-containing compounds produced from methanol, ethanol, and butylene fractions obtained from coal, gas, plant products, and heavy oil residues. Gasoline containing oxygenates is characterized by improved cleaning properties, combustion characteristics, and forms less carbon monoxide and hydrocarbons during combustion. A common feature for all oxygenates is low calorific value than hydrocarbons, therefore their amount in the fuel is limited by the ability of the engine to operate without additional adjustment. In average, the recommended concentration in gasoline is 3.0-15.0% and should be selected so that the oxygen content in the fuel not exceed 2.7% <sup>[5]</sup>.

Oxygenates (see Table 1) are characterized primarily by high octane mixing numbers, saturated vapor pressure, calorific value, and hygroscopicity. They are able to improve the antiwear properties of fuels even when contained in gasoline in concentrations of 0.05-0.10%. In practice, alcohols, esters, their mixtures, and waste from food and petrochemical industries are used as oxygenates.

Droportion	Oxygenates				
Properties	$C_5H_{12}O$	CH₃OH	$C_4H_{10}O$	C <sub>5</sub> H <sub>12</sub> O	
• · · •					
Oxygen content, %	18.2	49.9	21.6	22.4	
Molecular weight, g/mol	88.5	32.04	74.12	88.15	
Density at 15.5 °C, g/cm <sup>3</sup>	0.744	0.792	0.788	0.805	
Flash Point, °C	-25.6	11	14	20.5	
Boiling Point, °C	55	65	82	102	
Spontaneous combustion temperature, °C	460	455	490	425	
Saturated Vapor Pressure, kPa	53.8	31.7	5.5	1.6	
Octane number:					
- Motor method	101	92	100	100	
- Research method	116	107	130	130	

Table 1. Properties of some oxygenates [6]

2) **Fuel detergents** are able to wash away sediments in combustor of the engine and whole fuel system <sup>[7]</sup>. The main active components of fuel detergents are surfactants (surfactants). The additive with high surface - active properties must displace sediments from the surface, crush the particles of dirt in the fuel volume, and transfer them to a preserved state in order to remove dirt from the internal combustor. The additive must effectively counteract the formation of new resinous particles to prevent the formation of new sediments. Since one substance cannot perform all these functions well, fuel detergents consist of balanced composition of several compounds. The average concentration of detergent additives in fuel is within the range of up to 0.3 % <sup>[8]</sup>. Highly alkaline sulfonates, salicylates, calcium and magnesium phenolates are used as fuel detergents.

3) **Depressant additives** are used in diesel and boiler fuels and designed to improve fuel consumption at low ambient temperatures. Depressant additives are able to connect with dispersed solid hydrocarbon particles at the time of the dispersed phase in paraffin-containing systems formation by adsorption or integration of solid hydrocarbon crystals into the structure. In this case, there is a change of particles in the size, shape and structure (molecular structure) of the dispersed phase, and in some cases, increase in the solubility of solid hydrocarbons. And it contributes the energy barrier on the surface of solid phase particles due to repulsive forces of one nature or another, that prevents the gravity and coagulation of dispersed phase particles under certain conditions.

Depressant additives change their shape (paraffin crystals are rounded) and reduce their size by interacting with paraffin hydrocarbons. Side faces of crystals are blocked by adsorbed additives, and crystal growth occurs due to dislocations on their surface. The use of depressor additives in fuels is based on reducing the size of paraffin crystals in order to improve their filterability at low temperatures.

Currently depressor additives to diesel fuels are known by their chemical nature and can be classified as follows: ethylene copolymers with polar monomers (ethylene-vinyl acetate copolymers and their compositions, triple copolymers based on ethylene and vinyl acetate, ethylene copolymers with other polar monomers); polyolefin type products (ethylene-propylene copolymers, ethylene-propylene-diene and their degradation products, alpha-olefin copolymers, modified polyolefins); polymethacrylate additives (polyalkyl (met) acrylates, alkyl (met) acrylate copolymers); non-polymer chemicals (alkylnaphthalenes; esters of polyatomic acids and alcohols; amides containing long alkyl radicals). Depressant additives due to the mutual increase in positive properties are often combined with dispersants.

4) **Dispersants additives** are intended to maintain contamination of the fuel in dispersed state and prevent the formation of aggregates that can damage the internal combustion engine fuel system.

5) **Ignition promoters** are intended to improve the flammability of diesel fuels in the internal combustion engine combustion chamber, in other words, they affect the increase of cetane number (CN). The diesel fuel reduces the duration of cold start of the internal combustion engine and reduces the emission of smoke characteristic of the starting period adding the ignition promotes. The operational principle of inflammatory promoters is explained by the slight breakdown of their molecules (most often nitrates or peroxides) by the O-O and O-N bond with a low activation energy. Free radicals are formed and initiate fuel ignition. Additives of this type act only at the initial stages of the combustion process, that is why they are called ignition promoters. This type of additives are produced on the basis of: isopropyl nitrate; Cyclohexyl nitrate; di-ethylhexyl nitrate; alkyl peroxides <sup>[9]</sup>.

6) **Anti - wear additives** increase the lubricating characteristics of diesel fuels. This group of additives is usually represented by derivatives of phosphoric, phosphoric or dithiophosphoric acids, amides and ammonium salts of carboxylic acids or organometallic complexes. The content of such additives in fuel is in average ranges up to 5%.

#### Additional additives:

1) Antioxidant additives increase the oxidative stability of fuel during storage, prevent the formation of resins and sediment due to the oxidation of fuel hydrocarbons with air oxygen. Low-molecular oxidation products are peroxides, alcohols, acids and other oxygen-containing compounds have reaction with polymerization and polycondensation to form high-molecular products that are contained in the fuel in the form of resins or fall out of them in a separate phase. The more resins in the fuel, the more sediments are formed in the engine and fuel system. As a result, the processes of mixing and combustion become suboptimal: the pumpability and filterability of fuel deteriorate, there is a violation in the fuel combustion process, the efficiency of the internal combustion engine decreases, and the concentration of toxic products in the exhaust gases increases. The lower the oxidative stability of fuels, the shorter the permissible shelf life. Peroxides formed during the oxidation of gasoline reduce their ON, and the reduction can reach 5 units. Antioxidants inhibit only radical chain reactions: oxidation of hydrocarbons and partial polymerization of unsaturated compounds. However, in fuels containing active compounds of various nature (Diene and polycyclic aromatic hydrocarbons, nitrogen-containing heterocycles, etc.), other compaction reactions are also possible, leading to the formation of sediment and resins. This is especially true for medium distillate fractions obtained by destructive oil refining processes. The introduction of antioxidants in such fuels does not give the expected effect. Therefore antioxidants are mainly used to stabilize gasoline and jet fuels. The principle of action of antioxidants is based on breaking the chains of oxidation of hydrocarbons by interacting with radicals. The antioxidants used in fuels are spatially shielded phenols (see Table 2) and aromatic amines, sulfides, thiophosphates, some amines). The average concentration of antioxidants in gasoline is in the range of 0.05-0.10 % <sup>[8]</sup>.

2) **Combustion promoters** are the additives for improving the combustion process of gasoline and simultaneously reducing the emission of incomplete combustion fuel products into environment (nitrogen oxides, carbon monoxide, solid particles, as well as aromatic hydrocarbons) called as toxic substances. Salts of alkaline and alkaline earth metals, carboxylic and sulfonic acids, as well as hydrocarbon polymers (for example, polyisobutene) could be as combustion promoters. The average concentration of combustion promoters in fuels is within 0.02-0.15 % <sup>[9]</sup>.

Additive	Chemical Formula	MW, g/mol	Boiling point, °C	Scope of Application
AO-29	2,6-Di-Tert-Butyl-4-	220,356	265	Gasolines
AO-30	Methylphenol (C <sub>15</sub> H <sub>24</sub> O) 2,4-Dimethyl-6-Tert- Butylphenol (C <sub>12</sub> H <sub>18</sub> O) 2,4-Dimethyl-6-Tert-	170,2	249	Jet fuel and gasoline, including aviation gasoline
AO-32	Butylphenol + 2,6-Di-Tert-	170,2	249	Jet fuel and gasoline,
AU-32	Butyl-4-Methylphenol	220,35	265	including aviation gasoline
AO-37	$(C_{15}H_{24}O)$ 2,6-Di-Tert-Butylphenol $(C_{14}H_{22}O)$	206,329	253	Jet fuel and gasoline, aviation fuels

Table 2. Characteristics of antioxidant additives based on shielded phenols <sup>[10]</sup>

3) **Anti - smoke additives** reduce the concentration of smoke in the exhaust gases of diesel internal combustion engines. Anti-smoke additives are usually added into fuel at the location of use, but in many countries of the world it is possible to produce special brands of diesel fuel with anti-smoke additives at refineries. Anti-smoke additives enhance burning of soot in the combustion chamber until the end of main mass fuel combustion and the beginning of working mixture expansion stage. The effectiveness of such additives significantly depends on the type of engine and operating mode. The working concentrations of modern anti-smoke additives are 0.05-0.20%. Complex compounds containing barium, calcium or manganese are used as anti-smoke additives [9, 11].

4) **Anti - residue additives** reduce carbon residue at the internal combustion engine chamber, on valves and nozzle sprayers. The additive modifies the structure of carbon residue, gives catalytic effect on burnout and washes away carbon residue and products of transformation. In general, anti - residue additives are compositions of molybdenum - and zinc-containing compounds with a detergent-dispersing component or compositions of combustion catalyst (copper salt of organic acid), thermostable dispersing component, carbon residue modifier (oxygen-containing compounds) and a highly aromatized solvent. Recommended concentrations of anti residue additives with constant use are 0.005 - 0.02% <sup>[10]</sup>.

5) **Anti-soot additives** reduce the combustion temperature of soot burn at the filter surface and reduce clogging rate of diesel particulate filters. The additive ensure gradual burning of soot that eliminats the risk of overheating during periodic regeneration. Anti-soot additives are produced on the basis of fuel-soluble iron and copper compounds. The additives frequently include surfactants and ferrocene additives. Anti - soot additives can significantly reduce the oxidative stability of fuels by adding copper-and iron-containing additives and increase the toxicity of their combustion products. For this reason, additives are introduced into the fuel directly at the site of application, and it is not recommended to store fuel with additives for a long time. Recommended concentrations of anti-soot additives in fuels are 0.01-0.02% <sup>[11]</sup>.

6) **Antistatic additives** improve the ignition of jet and diesel fuels, prevent the formation of static electricity charges in fuels when pumped. Antistatic additives increase the electrical conductivity of fuels. The accumulation of static electricity is reduced and safety is ensured during refueling and pumping operations with jet and diesel fuel by increasing electrical conductivity. These additives are a mixture of chromium and cobalt derivatives of oleic acid and phenolic antioxidant. Recommended concentrations of antistatic additives in fuels are 0.005-0.01% <sup>[12]</sup>.

7) **Stabilization additives** can reduce the evaporation of gasoline during long-term storage. These substances on the surface of gasoline create structural bulk layers that prevent intense evaporation. These additives include compositions of surfactants: phthalates, alcohols, esters, ammonium salts containing fluorine. The optimal concentration of additives in gasoline is 0.001-0.01 % <sup>[8]</sup>.

8) **Biocide additives** prevent fuel spoilage with microorganisms. The main requirements for such additives include ensuring high efficiency at low concentrations and the absence of corrosive and toxic properties. Biocidal additives have an inhibitory effect on the growth of

bacteria, fungi and mold in hydrocarbon fuels. They are used to protect against bacterial activity in all liquid hydrocarbon fuels, including biofuels. Amine derivatives, copper sulfate, potassium permanganate and other compounds can be used as biocidal additives. The working concentrations of modern biocidal additives are up to 0.05% <sup>[13]</sup>.

Lubricating oils, as well as fuels, use anti-wear, anti-oxidation, depressant, detergent and dispersing additives. But this range, taking into account the functions of lubricating oils and their operating conditions, is supplemented with viscous, antifriction, anti-corrosion, anti-foam additives and revitalizants. The total amount of additives in commercial oil reaches 15-25% <sup>[14]</sup>.

Viscous (thickening) additives are high molecular polymers that have variable solubility in oil at different temperatures, so they increase the viscosity of the oil and reduce the change in viscosity during temperature change. Viscous additives thicken the oil less at low temperatures than at high temperatures. As additives of this type are used: polyisobutylene, polymethacrylate, styrene copolymers with dienes, olefin copolymers. In some cases antioxidant, dispersing or depressant properties, which reduces the content of the latter in the lubricant are given to viscous additives. The content of such additives in the oil varies within 10%.

**Antifriction additives** are introduced into oils except motor oils to reduce friction and increase engine efficiency. Usually this group of additives include solid finely dispersed molybdenum disulfide, colloidal graphite, polytetrafluoroethylene, metal acetates and borates, as well as oil-soluble fatty acid esters and organic molybdenum compounds. The mechanism of action is based on the adhesion of solid particles on lubricating surfaces and the formation of continuous layer with a low coefficient of friction. The disadvantage of solid friction modifiers is the possibility of their precipitation and capture on oil filters. The content of antifriction additives in the oil sometimes could reach up to 10%.

**Anticorrosive additives** are added to protect against corrosion damage and destruction of parts made of non - ferrous metal alloys-crankshaft bearing inserts with an anti-friction layer of lead bronze, connecting rod upper head bushings, etc. These additives are represented by dithiophosphates and dithiocarbonates of metals, alkylphenolic additives containing bound sulfide sulfur, and benzotriazole derivatives. The action mechanism of these additives is to form strong film of sulfides and phosphides, which are not destroyed during friction and under the action of detergents and do not dissolve in weak organic acids, the products of oil oxidation. The content of such additives in the oil ranges from 3.0 -5.0 %.

**Anti-foam additives** reduce oil tendency to foam. The addition of dispersants, detergents and other surfactants to the oil reduces the surface tension, and with a high multiplicity of oil circulation in the internal combustion engine and pressure drops, the foaming process occurs. The presence of anti-foam additive droplets in thin films of bubble-forming oil helps to break the bubbles and reduce foaming. As an anti-foam additive, silicone liquids finely dispersed in the volume of oil are usually used. Their content in the oil ranges from 0.002-0.005%.

**Revitalizant** is an additive that helps to restore new coating in the places of friction of internal combustion engine parts. The basis of this additive is natural material called cermet. The surface layer of the part is destroyed under the influence of loads in the friction zone. Metal atoms break off from the surface and move into the lubricant. The entire families of atoms called clucters can break off during overloads. When revitalizant enters the friction zone, it acts as catalyst for the growth of new surface, causing the process of carbon absorption by the surface layer, resulting in formation of metal carbides. New protective layer is formed in the excess energy zone with the participation of carbides and metal particles erased from the working surfaces located in the lubricant. At the final stage, due to the diffusion (physico-chemical process of penetration of molecules of one substance into another during friction or when perfectly polished surfaces are joined) of the protective layer into the metal, a strong cermet surface with unique operational properties is formed.

As for plastic lubricants, they use almost in lubricating oils, viscous, anti-corrosion, antifriction, anti-oxidation and anti-wear additives. The total amount in the composition of lubricants, unlike oils, usually does not exceed 5.0%. In some cases, when using lubricants under specific operating conditions, the additive package in the composition can be supplemented with adhesive and extreme pressure additives. Adhesive additives increase the ability of the lubricant to stay on vertical friction surfaces. Various amino derivatives such as alkyldiamines, alkylamidoamines, polyethylene polyamines, etc. are widely used as adhesive additives. Adhesive additives are very sensitive to shear stresses and high temperatures Due to their high molecular weight. The optimal concentration of adhesive additives in the composition of plastic lubricants is in the range of 0.5-2.0%. Table 3 shows the characteristics of adhesive additives by Afton Chemical, that are a combination of a high-molecular polymer in mineral oil.

Additive	Kinematic vis- cosity at 100°C	Density at 15°C, g/cm <sup>3</sup>	Flash point, °C	Solidification temperature, °C	Maximum operat- ing tempera- ture,°C
HiTEC 151	1200	0,870	150	-20	80
HiTEC 152	2850	0,875	155	-20	

Table 3. Characteristics of adhesive additives [15]

**Extreme pressure additive** prevent the appearance of jamming and scuffing on the surfaces of the friction pair. Extreme pressure additives are represented by potassium chlorides, potassium borates and phosphorus sulfides. Also, anti-wear additives can be sulfur-containing compounds that provide resistance to high loads and in some cases have good anti-wear properties. They are obtained by greasing olefins, fatty acid esters, esters and natural triglycerides, and the content of active or inactive sulfur is not less than 10 % (Table 4).

Additive	Chemical Base	Total sulfur content, %	Viscosity at 40°C, mm <sup>2</sup> /s	Welding load 10%	in SN 100, kg 15%
ROSCAN 741 E	Fatty Acid Esters	10	35	400	400
ROSCAN 1111	Fatty Acid Esters	11	250	400	500
SULFAD 1523E	Fatty Acid Esters and Triglycerides	15	275	500	500
ROSCAN 1115	Triglycerides of Plant Origin	15	315	500	500
ROSCAN 1215	Triglycerides of Plant Origin	15	530	400	500

Table 4. Characteristics of extreme pressure additives based on sulfur-containing esters and triglycerides <sup>[16]</sup>

The viscosity and solubility of additives depend on the types of organic compounds bound to sulfur. This, in turn, increases the lubricity, friction, wear and welding resistance of these substances. They react with the metal surface under heavy load, at low or high temperatures, forming physical barrier that eliminates metal-to-metal contact under extreme conditions. Extreme pressure additives prevent welding roughness of the contacting surfaces, reduce roughness and slow down the wear of friction surfaces. Extreme pressure additives are added to lubricants in amount of up to  $3.0 \ \% \ ^{16]}$ .

It should be noted that the existing range of additives should be supplemented with components such as dyes, that can be considered as additives. Currently the technical literature devoted to the use of additives in fuels and lubricants, the issue of using additives of this type, as per our opinion, is insufficiently elaboted and requires comprehensive research. The use of dyes in the production of petroleum products allows to create unique, branded fuel and lubricants (gasoline, aviation and diesel fuels, lubricating oils and plastic lubricants), label products with appropriate shades (from red to purple). It is possible to use dyes both in the production of petroleum products, and in the places of their application and storage. The scope of dyes use covers refineries, motor transport enterprises gas stations , warehouses of petroleum products, airline airfields; railway complexes, ports and repair bases.

The main directions of dye additives application in the production and use of fuel and lubricants are shown in the block diagram shown in Figure 2.



Figure 2. Directions of dyes application

Considering the direction of dyes application shown on Figure 2, note the following:

1) Identification of petroleum products, on the one hand, is one of the key issues of regulating the turnover of commercial petroleum products, in order to find out the need to pay of excise duty, on the other it is necessary to conduct forensic studies in the framework of criminal implementations.

2) Control of technological processes are directly related to the transportation of petroleum products, distribution to customers, storage, distribution, etc.

3) Protection Against Forgery is continuous monitoring of petroleum products throughout the entire process from producer to consumer. Prevention of petroleum products counterfeit or mixing them with other components.

4) Classification of petroleum products is very relevant for large producers of petroleum products with a wide range of products manufactured. It will also help to regulate commodity, transport operations and create a quality bank for petroleum products. Separation of military grades of fuel and lubricants from civilian.

5) Creating of branded petroleum products that belong to the premium class are characterized by a high level of operational properties.

6) Oil batch division products is necessary for commodity transport operations of petroleum products that differ in composition, purpose and properties, but included in the same delivery batch.

The main requirements for dyes used in petroleum products as additives can be presented in the form of a block diagram shown on Figure 3.



Figure 3. Dye Requirements

Stable dye composition (see Figure 3) is the ability to maintain original properties for a certain time, that is not to oxidize or decompose under the influence of operating conditions (air oxygen access, temperature and pressure), established during storage and transportation of petroleum products.

The ease of dye use in petroleum products involves their mixing with the latter without the use of special complex equipment. The safety of use requires the ratio of dyes to moderately or low - hazard substances (III or IV Hazard Class) and expressed in the absence of harmful effects of the dye on the human body and environment, while observing necessary safety rules. The dye should not significantly increase the cost of the final commercial product.

The dye must be compatible with other components of petroleum products, especially additives, and do not cause their decontamination that can lead to deterioration of petroleum products quality.

Among the key players operating in the global oil dye market such as: Innospec, Improchem, Sunbelt Corporation, John Hogg Technical Solutions, The Dow Chemical Company, United Color Manufacturing, Inc. and Authenticx, Inc. Today the dyes (markers) for petroleum products coloring in particular fuels are used as: Solvent Red 19 ( $C_{24}H_{21}N_5$ ); Solvent Red 26 ( $C_{25}H_{22}N_4O$ ); Solvent Blue 35 ( $C_{22}H_{26}N_2O_2$ ); Solvent Yellow 124 ( $C_{22}H_{31}N_3O_2$ ) <sup>[17-19]</sup>.

Usually, the content of these dyes in the composition of fuels does not exceed 0.2-0.5 %. The use of dyes in various types of fuel in different countries is shown in Table 5.

The dyes can be not only synthetic substances, but also of plant origin by their nature. Thus, in <sup>[21]</sup>, it was proposed to use vegetable dye obtained from *Rothmenia hispidia*, *Ptero-carpus osun*, and *Terminalia superba* to color gasoline, diesel, kerosene, and wax in Nigeria. On the basis of these plant dyes from yellow to orange and red colors were obtained.

To the above requirements for dyes (see Figure 3), in our opinion, it is necessary to add bifunctionality, that will add certain color to the oil product and improve its operational properties. For example automobile gasoline will be "color and detonation resistance"; diesel fuel will be "color and density" or "color and anti – wear properties"; lubricating oils and lubricants will be "color and anti-corrosion properties". Bifunctional dyes will reduce the use of additives that give the oil product same properties as the dye, and this will balance the additive package and reduce the cost of fuel and lubricants.

No	Fuel type	Dye brand (Marker)	Country
1.	Fuel with high sulfur content	Solvent Red 26 , Solvent Red 164	USA
2.	Gas oil / kerosene	Solvent Red 24 / Solvent Yellow 124	United Kingdom
3.	Diesel fuel / marine diesel fuel	Solvent Red 24 / Solvent Blue 35	France
4.	Fuel oil	Solvent Yellow 124	Austria
5.	Fuel oil	Solvent Yellow 124 + Solvent Red 19	Germany
6.	Fuel oil	Solvent Yellow 124	Finland
7.	Fuel oil /gas oil	Solvent Red 161 / Solvent Green 33	Italy
8.	Fuel oil / agricultural diesel fuel	Automate Red NR / Au- tomate Blue 8 GHF	Estonia
9.	Gas oil / kerosene	Solvent Yellow 124 /Solvent Red 19	Ireland
10.	Fuel oil	Solvent Blue 35/ Solvent Blue 79/ <u>Solvent Yellow</u> <u>124</u>	Sweden

Table 5. Use of Dyes in Fuels by Country [20]

## 4. Conclusions

The analysis of literature data has shown that use of additives in fuel and lubricants is the fastest and least expensive way to increase level of operational properties. Therefore, it can

be considered as the most rational in the geopolitical conditions that have developed around Ukraine today.

Today, the world market offers wide range of additives various in compositions and functional purposes. At the same time, additives for fuel and lubricants should be selected in a way that they do not only come into conflict with each other and as a result deactivated but also mutually increase their properties.

Dyes for adding color to fuel and lubricants should be considered as an integral component of the additive package. The use of dyes will simplify the procedure for identifying various batches of fuel and lubricants, create their own classification at manufacturing enterprises, ensure a high level of safety while using, increase protection against fraud, and make transportation, storage, and distribution of fuel and lubricants more convenient. The most promising dyes for fuel and lubricants are those that exhibit multifunctional properties. The use of such dyes will balance the additive packages to fuel and lubricants and reduce their cost by lowering the content of the corresponding additives.

#### References

- [1] TR TS 013/2011. Tekhnicheskiy Reglament Tamozhennogo Soyuza. O trebovaniyakh k avtomobil'nomu i aviatsionnomu benzinu, dizel'nomu i sudovomu toplivu, toplivu dlya reaktivnykh dvigateley i mazutu. Data vvedeniya 31.12.2012. Data aktualizatsii 01.01.2021. – 22s.
- [2] Silva LK, Espenship MF, Pine BN, Ashley DL, de Jesús VR, Blount BC. Methyl Tertiary-Butyl Ether Exposure from Gasoline in the U.S. Population, NHANES 2001–2012. Environ Health Perspect. 2019; 127(12): 127003.
- [3] Ure AD, Ghosh MK, Rappo M, Dauphin R, Dooley S. Rational Design and Testing of Anti-Knock Additives. Energies, 2020; 13: 4923.
- [4] Sheet EAE. Preparation of Gasoline Anti-knock Additives by Light Petroleum Products Fractionation. Journal of Applied Engineering Research. 2010; 5(11): 1905-1914.
- [5] DSTU 7687:2015 «Benzyny avtomobil'ni Evro. Tekhnichni umovy». DTS «UkrNDNTS», Kyyiv, 2015. 15s.
- [6] Soheil BS, Morteza SS, Fathollah O. Effect of Oxygenates Blending with Gasoline to Improve Fuel. Chinese journal of mechanical engineering, 2012; 25(4): 792-797.
- [7] Pereira A, dos Santos F, da Silva KK, d' Avila LA, Dweck Jo. Characterization of fuel detergent–dispersant additives by thermogravimetry. Journal of Thermal Analysis and Calorimetry, 2018; 131: 783–788.
- [8] Domantsevych NI. Kharakterystyka suchasnykh prysadok, dobavok ta dodatkiv do motornykh palyv. Visnyk L'vivs'koho torhovel'no-ekonomichnoho universytetu. Tekhnichni nauky. 2020; 24: 14-18.
- [9] Yarmolyuk BM, Korotkova NP, Bereza LI. Tendentsiyi zastosuvannya dodatkiv do benzyniv. Kataliz i naftokhimiya, 2006; 14: 53-70.
- [10] Fuel antioxidants". Innospec Chemicals. Archived from the original on 15 October 2006. Retrieved 27 February 2007.
- [11] Danylov AM. Prysadky do palyv. Khimiya ta tekhnolohiya palyv i masel, 2007; 2: 47-56.
- [12] Yadav A, Chakradhar M, Chopra A, Christopher J, Kapur GS. Estimation of Static Dissipater Additives in Aviation Turbine Fuels Using ASTM D7524 and ASTM D2624: Observation, Precautions, and Suggestions Thereof. Energy Fuels, 2018; 32(2): 1336–1339.
- [13] Yemel'yanov OI, Polyakova AV. Zashchita topliv i materialov toplivnykh sistem samoletov ot mikrobiologicheskogo porazheniya. Aviatsionnyye materialy i tekhnologi, 2004; 3: 90-95.
- [14] Shkol'nikov VM. Goryuchiye smazochnyye materialy. Entsiklopedicheskiy tolkovyy slovar'-spravochnik. Tekhinform. 2010, p. 756.
- [15] Tackiness & Adhesive Additives. Afton Chemical Corporation develops & manufactures petroleum additives, including driveline, engine oil, fuel, & industrial additives

https://www.aftonchemical.com/SBU/Lubricant-Components/TackinessAdditives.

- [16] Light-colored sulfurized esters ROSCAN & SULFAD. Chemical concern SEQENS: [ https://customspecialties.seqens.com/en/business-lines/products/lubricants-additives/
- [17] Morris RE, Beal E, Mitchell CS. The impact of red dye on the stability of marine diesel fuels. Petroleum Science and Technology, 1997; 15( 9-10): 907-919.
- [18] Timkovich R. Analysis of regulatory dye in diesel petroleum. Dyes and Pigments, 2000; 46( 2): 69-79.
- [19] Markevičius A, Zolumskis A, Sadaunykas A, Knašienė B, Claramunt AV, Šakirzanovas S, Naujalis E. Determination of dyes and marker in diesel using high performance liquid chromatography. Chemija, 2018; 29(2): 121–126.
- [20] <u>https://www.chemeurope.com/en/encyclopedia/Fuel\_dyes.html</u>
- [21] Ezeokonkwo MA, Okoro UC. New Dyes for Petroleum Products. Journal of Emerging Trends in Engineering and Applied Sciences, 2012; 3 (1): 8-11.

To whom correspondence should be addressed: Dr. Andrey Grigorov, National Technical University «Kharkov Polytechnic Institute», 61002, 2 Kirpichova str., Kharkov, Ukraine; <u>e-mail</u>: <u>grigorovandrey@ukr.net></u>