REPUBLIC OF AZERBAIJAN

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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

SYNTHESIS OF ESTERS OF (C_3–C_{10}) DICARBOXYLIC ACIDS AS A BASE AND COMPONENT OF LUBRICATING OILS AND STUDY OF THE TECHNOLOGICAL CHARACTERISTICS OF THE PROCESS

Speciality: 3303.01 – Chemical Technology and Engineering

Field of science: Chemistry

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GENERAL CHARACTERISTICS OF THE WORK

Relevance of the work and degree of development. With the advancement of technology, the requirements for lubricating oils are becoming increasingly stringent. To ensure that the quality of oils and fuels aligns with the demands of modern and advanced equipment, large-scale scientific research is being conducted. The required lubricants must have high thermal and thermal-oxidative stability, a high viscosity index and flash point, and good low-temperature properties[1].

Currently, approximately 90% of the oils in use are mineral oils. The performance and properties of mineral oils largely depend on temperature conditions: at high temperatures, the oils begin to burn out, while at low temperatures, their viscosity increases sharply, adversely affecting the operation of mechanisms. Mineral oils contain a significant number of foreign compounds, and this heterogeneity reduces their resistance to crystallization and liquefaction. Furthermore, during operation, mineral oils contribute to the formation of deposits, which significantly reduces engine performance and shortens its service life.

Since mineral oils do not meet the specified requirements, the development and use of synthetic oils with various chemical structures are of great relevance.

Among the promising chemical compounds used as lubricating oils are esters of dicarboxylic acids. These compounds are utilized both as base oils and as components of lubricating materials[2].

Esters of dicarboxylic acids are highly soluble in mineral oils and have several advantages over them, which are attributed to the presence of polar ester groups in their molecules.

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[1] Мамедъяров, М.А. Синтетические смазочные масла (структура и свойства) / М.А. Мамедъяров, Ф.Х. Алиева, Г.Н. Гурбанов, – Москва: Научный мир, – 2017, – 336 с.

[2] Gryglewicz, S., Oko F.A. Dicarboxylic acid esters as components of modern synthetic oils // Industrial Lubrication and Tribology, – 2005, Vol. 57, Issue 3, – p. 128-132.

These advantages include high viscosity-temperature characteristics (especially at low temperatures) and lubricating properties, high thermo-oxidative stability, a low pour point, and excellent biodegradability, which is of significant ecological importance today.

Since synthetic oils significantly surpass mineral oils in quality, thereby extending the service life of machinery and equipment, the scope of application for synthetic lubricating oils based on esters of dicarboxylic acids (instrument, compressor, motor, transmission, special-purpose oils, etc.) is expanding, leading to increased demand for such products.

Ester compounds are also used as fuel additives, reducing the amount of sediment formed during oxidation and improving fuel quality. Additionally, esters of dicarboxylic acids play an important role as plasticizers in polymer materials.

However, the currently used synthetic ester oils do not meet some of the requirements of modern technology. For example, these oils are less effective at dissolving additives compared to mineral oils.

On the other hand, the production of synthetic base oils requires a number of different manufacturing processes, which results in their extremely high cost compared to mineral oils.

In light of the above, the synthesis of new types of esters, the creation of lubricating oils based on them, and their investigation as components of fuels and mineral oils is a relevant and in-demand task.

Object and subject of work. The object of the study comprises mono-, symmetrical, unsymmetrical and complex esters synthesized from dicarboxylic acids (malonic, succinic, adipic, and sebacic) and alcohols of various structures (aliphatic, cyclic, and aromatic).

The subject of the research includes studying the possibility of using synthesized esters as a base and components of lubricating oils, additives to diesel fuels and polymers, corrosion inhibitors in preservation fluids, as well as bactericidal inhibitors.

The aim and objectives of the dissertation work. The aim of the research work is the synthesis and study of the physicochemical, viscosity-temperature, and operational characteristics of esters of (C_3–C_{10}) dicarboxylic acids of various structures, the preparation and study of the properties of compositions obtained by adding these esters to fuels and mineral oils, the development of a technology for obtaining esters and the optimization of the esterification process.

To achieve this goal, the following tasks were solved:

- synthesis and identification of mono-, symmetrical, unsymmetrical and complex esters of (C_3–C_{10}) dicarboxylic acids;
- study of the physicochemical and viscosity-temperature properties of the obtained compounds;
- study of the specific electrical conductivity of the synthesized esters depending on their chemical structure;
- research of the thermal stability of the synthesized esters of dicarboxylic acids;
- study of the bactericidal properties of the synthesized esters;
- creation and investigation of properties of compositions based on mineral oils and synthesized esters;
- preparation of 3% and 10% compositions based on synthesized esters with T-30 mineral oil and their study as a component of preservation fluids;
- use of synthesized symmetrical and unsymmetrical diesters as plasticizers in various polymer matrices and study of the plasticizing properties of the obtained polymer materials;
- study of the synthesized esters of dicarboxylic acids as antioxidants for hydrotreated diesel fuel;
- calculation-experimental method for selecting the optimal viscosity-temperature characteristics of lubricating oil compositions based on synthesized esters and T-46 mineral oil;
- finding optimal conditions for the succinic acid esterification process using computer modeling;
- development of the technological scheme for the production of esters of (C_3–C_{10}) dicarboxylic acids.

Research Methods. The esterification process was carried out under laboratory conditions in the presence of acidic heterogeneous catalysts. The structures of the synthesized esters were identified using FT-IR and NMR spectroscopy.

The kinematic viscosity of the esters was determined by measuring the efflux time of a known volume of the sample through a calibrated glass capillary viscometer. Dynamic viscosity was investigated using a rotational viscometer (on the “Reotest-2” apparatus) at speeds ranging from 9 to 243 rpm.

The obtained esters were studied as components of preservation fluids in various aggressive environments (automatically controlled experimental chamber “*CORROSIONBOX-1000E*”, hydrochamber “Г-4”, sea water, and 0.001% sulfuric acid solution), as antioxidants for diesel fuel in the "ЛСАРТ" apparatus, as bactericidal inhibitors against sulfate-reducing bacteria using strain 1143 of the species “*Desulfovibrio desulfuricans*” in the presence of the nutrient medium “Postgate B”, and as plasticizers by mixing them with various polymer matrices using a mixing roller, pressing, and determining the mechanical properties of the corresponding samples with a tensile testing machine.

Thermogravimetric analysis of the samples was carried out on a synchronous thermoanalyzer TQ/DTA STA-449.

The main provisions put forward for defense:

- diesters of (C_3–C_{10}) dicarboxylic acids of various structures have been synthesized and studied as a base for lubricating oils;
- mono- and diesters of (C_3–C_{10}) dicarboxylic acids have been studied as components of preservation fluids;
- the correlation between the structure of symmetrical, unsymmetrical, and complex esters of (C_3–C_{10}) dibasic acids and their viscosity-temperature properties has been established;
- the synthesized esters have been studied as antioxidant additives for hydrotreated diesel fuel;
- the bactericidal properties of esters of (C_3–C_{10}) dicarboxylic acids have been studied;

- the synthesized esters of (C_3–C_{10}) dicarboxylic acids have been studied as plasticizers for various polymer matrices;
- a technological scheme for the production of complex esters of (C_3–C_{10}) dibasic acids has been developed.

Scientific novelty of the dissertation:

- Symmetrical, unsymmetrical, and complex esters of (C_3–C_{10}) dicarboxylic acids were synthesized in the presence of KU-2-8 and Tseokar-2 catalysts and a correlation between the chemical structure of the synthesized compounds and their operational properties was established;
- On the basis of mono- and diesters of (C_3–C_{10}) dicarboxylic acids and mineral oil T-30, 3% and 10% compositions were prepared. These compositions were subsequently studied as components of preservation fluids and demonstrated excellent anticorrosion properties;
- the synthesized esters of (C_3–C_{10}) dicarboxylic acids were tested for the first time as antioxidant additives to hydrotreated diesel fuel and exhibited high antioxidant properties;
- mono-, di- and complex esters of (C_3–C_{10}) dicarboxylic acids were studied for the first time as bactericidal inhibitors against sulfate-reducing bacteria and high bactericidal properties were found;
- symmetrical and unsymmetrical esters of (C_3–C_{10}) dicarboxylic acids were studied as plasticizers for polypropylene, polyvinyl chloride and high-density polyethylene and good plasticizing properties were discovered.

The results of the dissertation work are confirmed by 3 patents of the Republic of Azerbaijan and 2 test reports.

Theoretical and practical significance of the work:

- synthesized esters of (C_3–C_{10}) dicarboxylic acids can be used as the base for instrument, hydraulic, and industrial oils;
- based on monoesters and mineral turbine oil T-30, 3% and 10% lubricating compositions were prepared, which

demonstrate a high anti-corrosion effect and are recommended as preservation fluids;

- due to the high antioxidant capacity, unsymmetrical esters of malonic acid (butyl-heptyl malonate, butyl-octyl malonate), succinic acid, and adipic acid (butyl-octyl adipate, heptyl-octyl adipate, diethylene glycol dicaproate adipate) were recommended as additives to enhance the antioxidant properties of diesel fuel;
- some esters (dioctyl malonate, di-4-methylcyclohexyladipate and di-4-methylcyclohexylsebacate), having good plasticizing properties, are recommended as plasticizers for PVC and PP;
- for the first time, all symmetrical esters of malonic acid, some monoesters of succinic and adipic acids, esters of sebacic acid at sufficiently low concentrations have a high protective effect and therefore were recommended as bactericidal inhibitors against sulfate-reducing bacteria.

The personal contribution of the author includes performing experimental work, collecting and analyzing literary data. The systematization, interpretation, and generalization of the research results were carried out with the direct participation of the author.

Approbation and implementation. A total of 28 scientific papers have been published on the topic of the dissertation, including 12 articles (six published in foreign journals), 13 abstracts presented at international and national scientific conferences, and 3 patents of the Republic of Azerbaijan.

The main results of the dissertation research were presented and discussed in the form of oral and poster presentations at international and national scientific conferences:

International Scientific Conference “Actual Problems of Modern Chemistry” dedicated to the 90th anniversary of the Institute of Petrochemical Processes named after Academician Y.H. Mammadaliyev (Baku, 2019); 32nd National Chemistry Congress (Turkey, 2020); Republic Scientific Practical Conference “Problems of Modern Chemistry and Development Tendencies” (Baku, 2020); Usbik 2021 Online International Congress on Natural Sciences (Turkey, 2021); 6th International Turkic World Conference on

Chemical Sciences and Technologies (Baku, 2022); “Lomonosov” International Scientific Conference for Students, Postgraduates, and Young Scientists (Baku, 2023); Conference “Petroleum chemistry, synthesis of polyfunctional monomers, oligomers and polymers” dedicated to the 90th anniversary of Academician Sahib Museyib oglu Aliyev (Baku, 2023); International scientific conference “Modern problems of petrochemistry and oil technology” dedicated to the 100th anniversary of Academician Maharram Ali oglu Mammadyarov (Baku, 2024), International Scientific Conference “Monomers and modern problems of petrochemistry” dedicated to the 100th Anniversary of the Academician Soltan Mehdiyev.

Place of the dissertation work. The work was carried out in the laboratory “Synthetic oils” of the Institute of Petrochemical Processes named after Academician Y.H. Mammadaliyev Ministry of Science and Education of Azerbaijan.

The total volume of the dissertation indicating the volume of structural sections. The dissertation is 200 pages long and consists of an introduction (12701 characters), four chapters (Chapter I – 52427, Chapter II – 35973, Chapter III – 44901, Chapter IV – 22925 characters, excluding spaces), conclusions (3304 characters), a bibliography with 198 citations, appendices and abbreviations. The dissertation includes 36 figures, 45 tables, and 1 scheme. The total volume of the dissertation is 172231 characters, excluding spaces, tables, figures, graphs, appendices, and the bibliography.

The introduction highlights the relevance and the degree of development of the scientific research, the aim and objectives of the study, the object and subject of the research, its scientific novelty, the approbation of the work, and its theoretical and practical significance.

The first chapter describes the analysis of the review of lubricants based on esters of dicarboxylic acids and considers the areas of their application.

The second chapter presents the synthesis, identification methods, physicochemical properties, and an analysis of specific conductivity measurements of (C_3–C_{10}) dicarboxylic acid esters depending on their structure. The optimization of the esterification process is also addressed.

The third chapter investigates the viscosity-temperature, operational characteristics of (C_3–C_{10}) dicarboxylic acid esters and studies the dependence of these properties on the chemical structure of the esters. Data on the optimization of the viscosity-temperature properties of compositions based on diesters of succinic and adipic acids with mineral oil T-46 are provided. A technological scheme for producing complex esters of (C_3–C_{10}) dicarboxylic acids, exemplified by an unsymmetrical ester of malonic acid, has been developed. Additionally, a techno-economic assessment of the synthesis of dibutyl malonate has been conducted.

The fourth chapter demonstrates the potential applications of the synthesized compounds and presents research findings on the antioxidant, anticorrosive, bactericidal, and plasticizing properties of the esters.

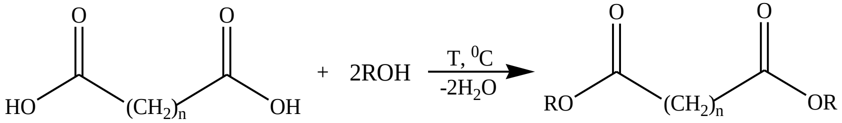
At the end of the scientific dissertation, the conclusions, reference list, appendices, and list of abbreviations are presented.

MAIN CONTENT OF THE WORK

In this dissertation, the synthesis of (C_3–C_{10}) dicarboxylic acid esters of various structures is carried out, their physicochemical, viscosity-temperature, operational, as well as bactericidal, and plasticizing properties were studied. The structures of the synthesized compounds were confirmed by IR and NMR spectroscopy. Based on the obtained esters and mineral oils of the T-30, T-46 and AK-15 brands, various compositions were prepared, their anticorrosive, antioxidant and lubricating properties were investigated.

Esters of (C_3 – C_{10}) dicarboxylic acids: synthesis and identification methods

The synthesis of *symmetrical esters* was carried out at an acid to alcohol ratio of 1:2 and 1:3, using a 1.5% catalyst (Tseokar-2, KU-2-8) in *para*-xylene medium. The general scheme of the esterification process is as follows:



where n = 1, 2, 4, 8; R = C_4H_9; *i*-C_4H_9; *i*-C_5H_{11}; C_7H_{15}; C_8H_{17}; C_9H_{19}; $C_{10}H_{21}$; CH_3-C_6H_{10}; C_6H_5-CH_2.

The end of the esterification was determined by the acid number and the amount of water released. Upon completion of the process, the esters were distilled under vacuum (2 – 3 mm Hg). The identification of the obtained products was carried out using IR and NMR spectroscopy methods. The spectra of the synthesized symmetrical esters are shown in Fig. 1 and 2.

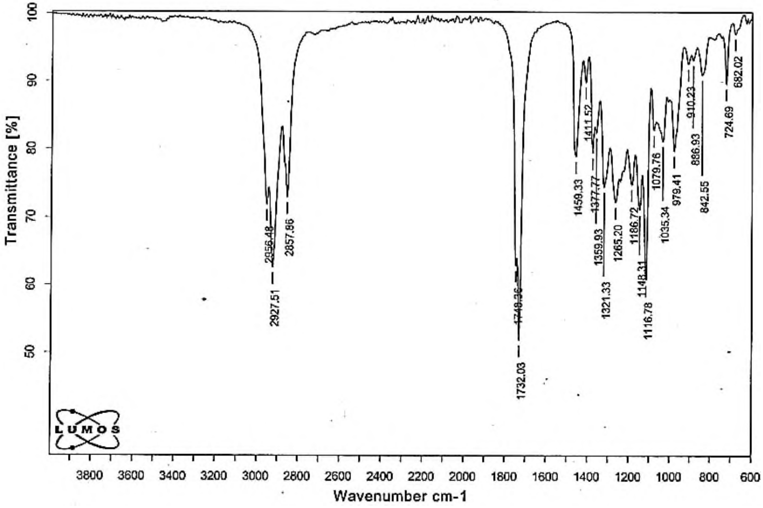


Fig. 1. IR spectrum of dioctyl malonate

The spectrum shows absorption bands characteristic of deformation (724, 1377, 1411, 1459 cm^{-1}) and stretching (2857, 2927, 2956 cm^{-1}) vibrations of the C–H bonds in the CH_3 and CH_2 groups. The stretching vibrations of the C–O bond of the ester are observed at frequencies of 1116 and 1148 cm^{-1}. The maxima at 1732 and 1748 cm^{-1} correspond to the stretching vibrations of the C=O bond of the ester.

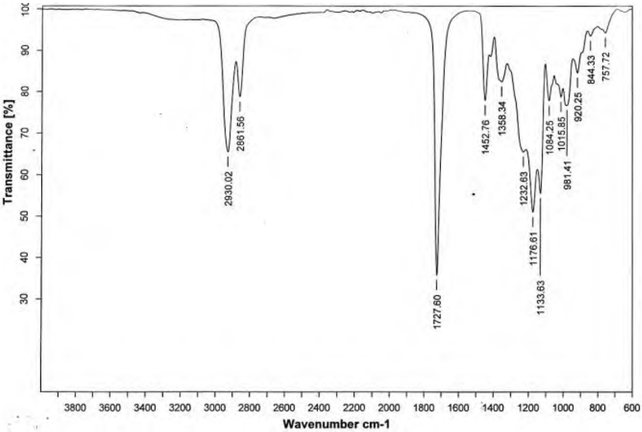
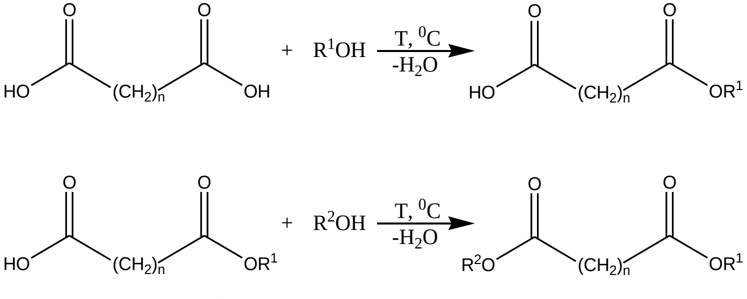


Fig. 2. IR spectrum of di(4-methylcyclohexyl)adipate

In the IR spectrum, low-intensity absorption bands of deformation and stretching vibrations of the C–H bonds in the CH_3 and CH_2 groups are observed at 1358, 1452 cm^{-1} and 2861, 2930 cm^{-1}, respectively. The peak at 981 cm^{-1} corresponds to the deformation vibrations of the C–H bond of CH_2 groups in the cycle. Peaks with frequencies of 1133 and 1176 cm^{-1} are characteristic of the stretching vibrations of the C–O bond of the ester. An intense absorption band of the C=O bond of the ester was detected at a frequency of 1727 cm^{-1}.

Unsymmetrical esters were synthesized stepwise: first, a monoester was obtained at an acid-to-alcohol ratio of 1:1, which was then esterified with another alcohol (1:1) in the presence of the KU-2-8 catalyst. The overall reaction scheme is as follows:



where n = 1, 2, 4, 8; $R^1 = C_4H_9$; C_7H_{15}; $CH_3\text{-}C_6H_{10}$; $C_6H_5\text{-}CH_2$
$R^2 = i\text{-}C_4H_9$; C_7H_{15}; C_8H_{17}; $C_{10}H_{21}$.

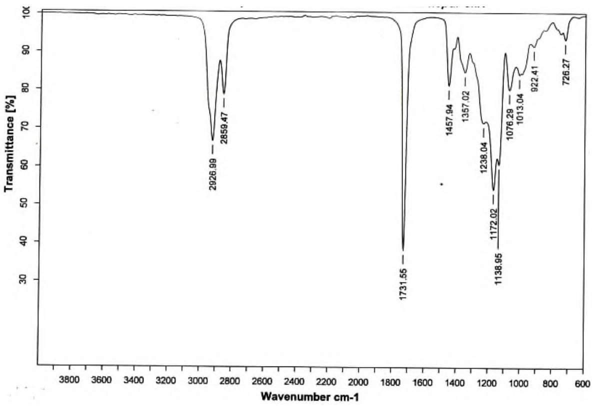


Fig. 3. IR spectrum of 4-methylcyclohexyl-heptyl adipate

The spectrum shows deformation (1357, 1457 cm^{-1}) and stretching (2859, 2926 cm^{-1}) vibrations of the C–H bonds of the CH_3 and CH_2 groups. The absorption band at 1731 cm^{-1} corresponds to the stretching vibrations of the C=O bond of the ester. The stretching vibrations of the C–O bond of the ester appear at frequencies of 1138 and 1172 cm^{-1}.

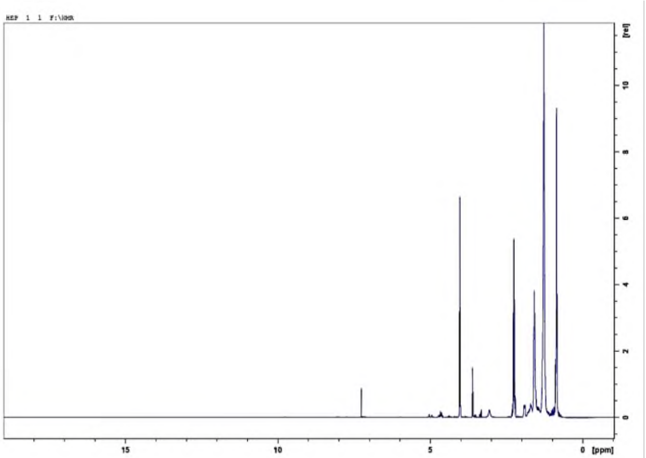


Fig. 4. NMR ^{1}H spectrum of 4-methylcyclohexyl-heptyl sebacate

The following signals are observed in the ^{1}H NMR spectrum (δ, ppm): 0.83-0.92 (m., CH_3), 1.18-1.33 (m., CH_2), 1.55-1.64 (m., CH_2), 1.68-1.74 (m., CH), 1.88-1.98 (m., CH_2), 2.21-2.32 (m., CH_2-C=O), 3.56-3.65 (m., OCH), 4.03 (t., OCH_2).

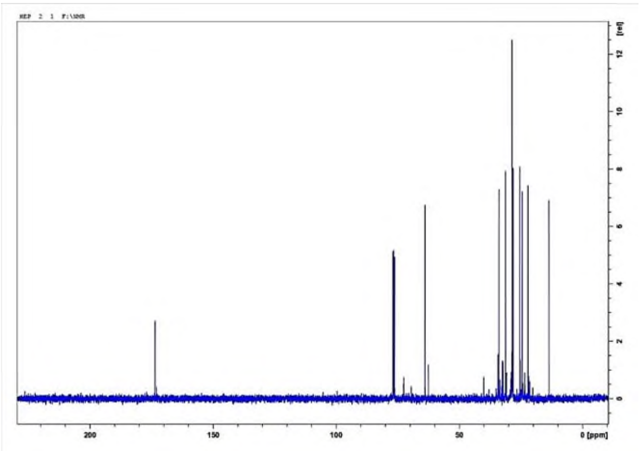
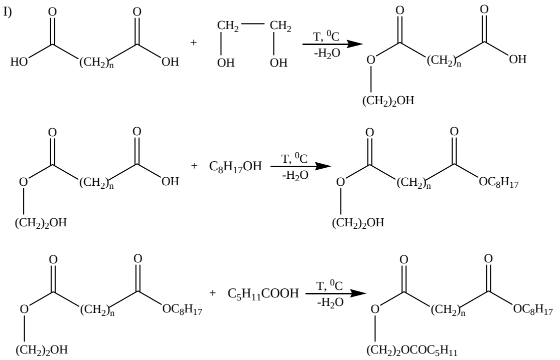


Fig. 5. NMR ^{13}C spectrum of 4-methylcyclohexyl-heptyl sebacate

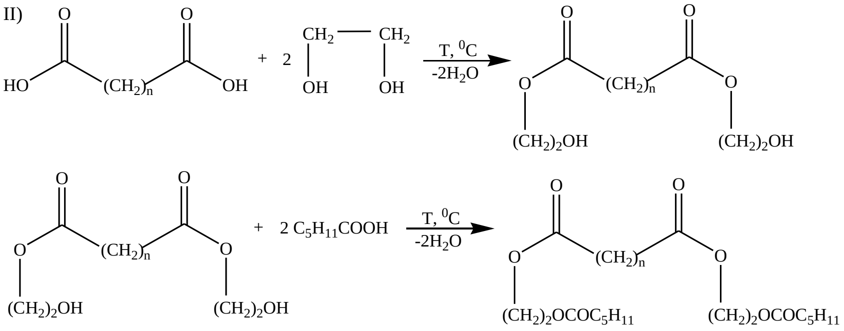
In the ^{13}C NMR spectrum (Bruker Avance 400, $CDCl_3$, δ, ppm), the following signals are observed: 13.63 (CH_3), 22.14, 25.45, 28.20, 28.48, 28.64, 31.29 (CH_2), 32.10 (CH), 33.92 (CH_2), 62.54 (OCH), 63.98 (OCH_2), 173.56 (C=O).

The synthesis of complex esters with 3 and 4 ester groups was carried out stepwise. To obtain esters with 3 ester groups (I), a monoester was first synthesized at an acid-to-ethylene glycol ratio of 1:1. This monoester was then esterified with octanol-1 (1:1) in the presence of the KU-2-8 catalyst. At the final stage, the obtained unsymmetrical ester was subjected to esterification with caproic acid. The general scheme of the synthesis is shown below:



where n = 2, 4, 8

To synthesize esters with 4 ester groups (II), a diglycol ester was first obtained at an acid-to-ethylene glycol ratio of 1:2. This diglycol ester was then esterified with caproic acid. The overall esterification scheme is given below:



where n = 2, 4, 8

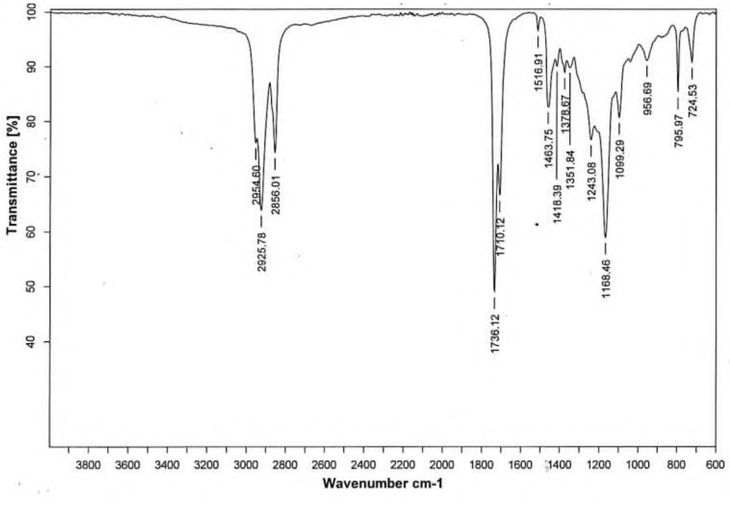


Fig. 6. IR spectrum of the complex ester of sebacic acid (ester 36)

The IR spectrum contains absorption bands of deformation (724, 1378, 1463 cm^{-1}) and stretching (2856, 2925, 2954 cm^{-1}) vibrations of the C-H bonds in CH_3 and CH_2 groups. Absorption bands at 1168 and 1736 cm^{-1} are inherent to the stretching vibrations of the C–O and C=O bonds of the ester, respectively.

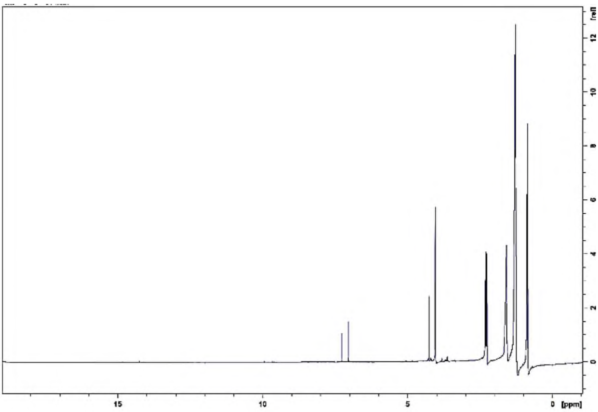


Fig. 7. NMR ^{1}H spectrum of the complex ester of sebacic acid (ester 36)

The following signals were detected in the ^{1}H NMR spectrum (δ, ppm): 0.84-0.93 (m., CH_3), 1.21-1.36 (m., CH_2), 1.56-1.60 (m., CH_2), 2.23-3.22 (m., CH_2-C=O), 4.04 (t., OCH_2), 4.26 (s., OCH_2).

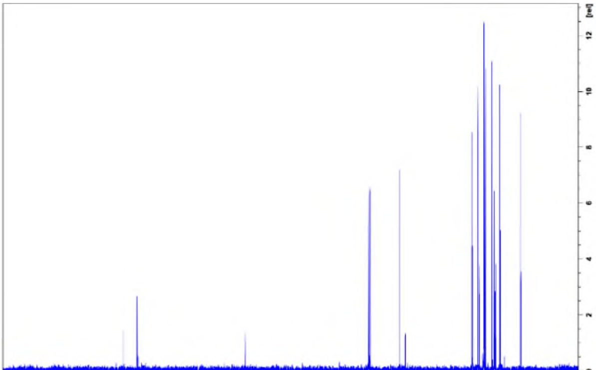


Fig. 8. NMR ^{13}C spectrum of the complex ester of sebacic acid (ester 36)

In the ^{13}C NMR spectrum (Bruker Avance 400, $CDCl_3$, δ, ppm) of the complex ester of sebacic acid, the following signals are observed: 13.65 (CH_3), 21.87, 22.21, 23.95, 24.53, 25.50, 28.20, 28.63, 30.78, 31.35, 33.57, 33.93 (CH_2), 61.59, 64.01 (OCH_2), 173.61, 179.21 (C=O).

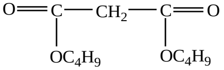
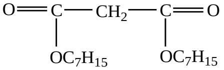
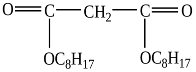
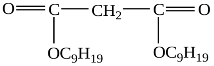
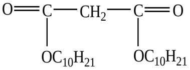
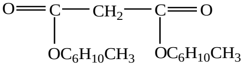
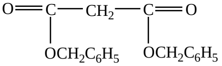
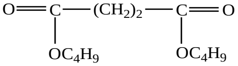
Study of viscosity-temperature properties of esters of (C_3-C_{10}) dicarboxylic acids

The study of the synthesized esters as lubricants was conducted in two stages: preliminary and in-depth. During the preliminary tests, the dependence of kinematic viscosity on temperature at 40°C and 100°C, the pour point and the flash point in an open cup were determined. Compounds that demonstrated satisfactory characteristics were subjected to a more detailed analysis, including the evaluation of their lubricating properties and thermo-oxidative stability.

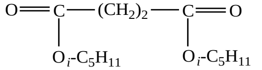
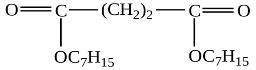
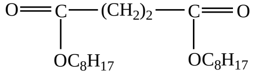
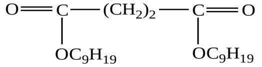
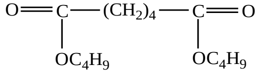
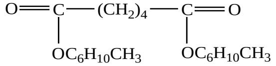
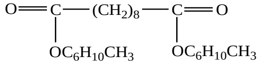
The viscosity-temperature properties of symmetric esters of (C_3-C_{10}) dicarboxylic acids are presented in Table 1.

Table 1

Viscosity-temperature characteristics of symmetric esters of (C_3-C_{10}) dicarboxylic acids

No.	Ester	Acid number, mgKOH/g	Kinematic viscosity, mm^2/s		VI	Pour point, °C	Flash point, °C
			100°C	40°C			
1	2	3	4	5	6	7	8
1	 $O{=}C(OC_4H_9)-CH_2-C(OC_4H_9){=}O$	1.28	1.13	2.30	96	-66	94
2	 $O{=}C(OC_7H_{15})-CH_2-C(OC_7H_{15}){=}O$	1.31	1.91	4.75	100	-63	157
3	 $O{=}C(OC_8H_{17})-CH_2-C(OC_8H_{17}){=}O$	1.60	2.02	5.84	158	-28	174
4	 $O{=}C(OC_9H_{19})-CH_2-C(OC_9H_{19}){=}O$	1.64	2.43	7.14	191	-17	180
5	 $O{=}C(OC_{10}H_{21})-CH_2-C(OC_{10}H_{21}){=}O$	0.11	2.64	7.69	214	-10	187
6	 $O{=}C(OC_6H_{10}CH_3)-CH_2-C(OC_6H_{10}CH_3){=}O$	2.12	1.52	3.47	92	-52	173
7	 $O{=}C(OCH_2C_6H_5)-CH_2-C(OCH_2C_6H_5){=}O$	1.24	1.45	3.27	87	-46	113
8	 $O{=}C(OC_4H_9)-(CH_2)_2-C(OC_4H_9){=}O$	1.0	1.40	3.09	93	-41	144

Continuation of Table 1

1	2	3	4	5	6	7	8
9	 $O{=}C(O_i\text{-}C_5H_{11})-(CH_2)_2-C(O_i\text{-}C_5H_{11}){=}O$	3.0	1.65	4.01	73	-60	127
10	 $O{=}C(OC_7H_{15})-(CH_2)_2-C(OC_7H_{15}){=}O$	2.0	2.13	5.55	250	-33	157
11	 $O{=}C(OC_8H_{17})-(CH_2)_2-C(OC_8H_{17}){=}O$	1.20	2.30	6.58	196	-24	168
12	 $O{=}C(OC_9H_{19})-(CH_2)_2-C(OC_9H_{19}){=}O$	2.20	2.55	7.60	193	-12	182
13	 $O{=}C(OC_4H_9)-(CH_2)_4-C(OC_4H_9){=}O$	1.05	2.30	6.95	163	-36	112
14	 $O{=}C(OC_6H_{10}CH_3)-(CH_2)_4-C(OC_6H_{10}CH_3){=}O$	1.10	4.72	26.28	95	-44	184
15	 $O{=}C(OC_6H_{10}CH_3)-(CH_2)_8-C(OC_6H_{10}CH_3){=}O$	2.75	6.38	29.32	178	-28	195
РЖ-8		0.03	-	6-7.5	-	-10	120
AVISTA HYD HLP 10		-	2.7	9.7	98	-33	170

According to the obtained data, in symmetrical esters, such as malonic acid esters, exhibit an increase in kinematic viscosity, viscosity index (VI), as well as pour point and flash point is observed with the elongation of the aliphatic radical. For instance, transitioning from the dibutyl ester to the didecyl ester results in an increase in kinematic viscosity at 100°C from 1.13 to 2.64 mm²/s and at 40°C from 2.30 to 7.69 mm²/s. The viscosity index increases from 96 to 214 points, the flash point from 94 to 187°C, and the pour point from -66 to -10°C.

In symmetrical esters of (C_3–C_{10}) dicarboxylic acids with a cyclic radical, a regular increase in viscosity index, pour point, and flash point is observed as the carbon chain of the acid lengthens. Thus, a comparative analysis of the viscosity-temperature characteristics of di-4-methylcyclohexyl esters of malonic, adipic, and sebacic acids shows that, as the acid changes from malonic to sebacic, the viscosity index increases from 92 to 178, the pour point – from -52 to -28°C, and the flash point – from 173 to 195°C.

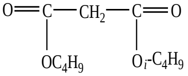
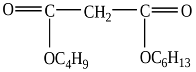
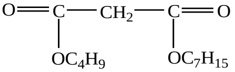
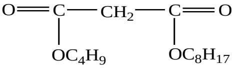
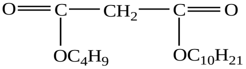
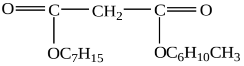
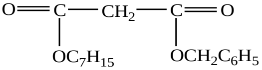
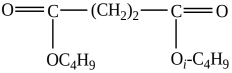
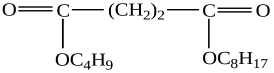
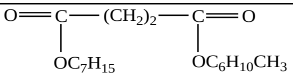
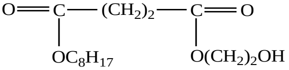
As can be seen from Table 1, the synthesized symmetrical esters of (C_3–C_{10}) dicarboxylic acids are not inferior to *AVISTA HYD*

HLP 10 hydraulic oil in terms of viscosity-temperature properties, and many of them surpass it in VI, pour point and flash point.

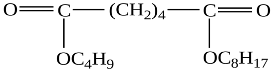
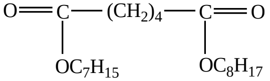
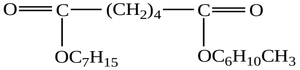
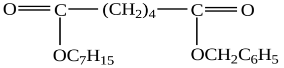
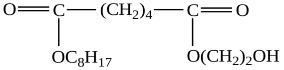
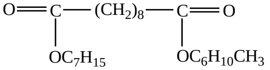
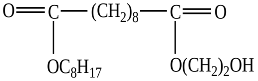
The viscosity-temperature properties of the unsymmetrical esters of (C_3–C_{10}) dicarboxylic acids are presented in Table 2.

Table 2.

Viscosity-temperature characteristics of unsymmetrical esters of (C_3-C_{10}) dicarboxylic acids

No.	Ester	Acid number, mgKOH/g	Kinematic viscosity, mm^2/s		VI	Pour point, °C	Flash point, °C
			100°C	40°C			
1	2	3	4	5	6	7	8
16	 $O{=}C(OC_4H_9){-}CH_2{-}C(O_{i}\text{-}C_4H_9){=}O$	2.43	0.99	1.97	82	-64	128
17	 $O{=}C(OC_4H_9){-}CH_2{-}C(OC_6H_{13}){=}O$	2.38	1.55	3.70	67	-54	154
18	 $O{=}C(OC_4H_9){-}CH_2{-}C(OC_7H_{15}){=}O$	2.23	1.87	4.68	90	-58	161
19	 $O{=}C(OC_4H_9){-}CH_2{-}C(OC_8H_{17}){=}O$	0.77	2.01	5.67	173	-31	172
20	 $O{=}C(OC_4H_9){-}CH_2{-}C(OC_{10}H_{21}){=}O$	0.65	2.62	7.51	222	-25	185
21	 $O{=}C(OC_7H_{15}){-}CH_2{-}C(OC_6H_{10}CH_3){=}O$	2.76	1.55	3.56	93	-50	165
22	 $O{=}C(OC_7H_{15}){-}CH_2{-}C(OCH_2C_6H_5){=}O$	3.52	1.49	3.45	77	-48	149
23	 $O{=}C(OC_4H_9){-}(CH_2)_2{-}C(O_{i}\text{-}C_4H_9){=}O$	2.65	1.50	3.37	99	-66	138
24	 $O{=}C(OC_4H_9){-}(CH_2)_2{-}C(OC_8H_{17}){=}O$	1.80	2.07	6.52	116	-40	160
25	 $O{=}C(OC_7H_{15}){-}(CH_2)_2{-}C(OC_6H_{10}CH_3){=}O$	1.34	2.05	6.46	113	-46	174
26	 $O{=}C(OC_8H_{17}){-}(CH_2)_2{-}C(O(CH_2)_2OH){=}O$	3.89	2.53	7.49	195	-14	207

Continuation of Table 2

1	2	3	4	5	6	7	8
27	 $O{=}\underset{OC_4H_9}{\underset{\vert}{C}}-(CH_2)_4-\underset{OC_8H_{17}}{\underset{\vert}{C}}{=}O$	1.60	2.48	7.32	193	-34	192
28	 $O{=}\underset{OC_7H_{15}}{\underset{\vert}{C}}-(CH_2)_4-\underset{OC_8H_{17}}{\underset{\vert}{C}}{=}O$	0.90	2.73	7.56	253	-58	204
29	 $O{=}\underset{OC_7H_{15}}{\underset{\vert}{C}}-(CH_2)_4-\underset{OC_6H_{10}CH_3}{\underset{\vert}{C}}{=}O$	2.30	2.96	8.88	220	-40	180
30	 $O{=}\underset{OC_7H_{15}}{\underset{\vert}{C}}-(CH_2)_4-\underset{OCH_2C_6H_5}{\underset{\vert}{C}}{=}O$	0.84	2.32	7.57	126	-42	176
31	 $O{=}\underset{OC_8H_{17}}{\underset{\vert}{C}}-(CH_2)_4-\underset{O(CH_2)_2OH}{\underset{\vert}{C}}{=}O$	3.55	2.96	9.21	201	-10	220
32	 $O{=}\underset{OC_7H_{15}}{\underset{\vert}{C}}-(CH_2)_8-\underset{OC_6H_{10}CH_3}{\underset{\vert}{C}}{=}O$	1.82	3.68	11.34	247	-36	200
33	 $O{=}\underset{OC_8H_{17}}{\underset{\vert}{C}}-(CH_2)_8-\underset{O(CH_2)_2OH}{\underset{\vert}{C}}{=}O$	4.01	3.41	10.96	212	-7	238
ИПМ-10		0.02	3	9.3-10.5	95-100	-50	150
Industrial oil И-5-А		0.02	-	6-8	-	-18	140

A comparison of unsymmetrical esters of (C_3–C_{10}) dibasic acids with a cyclic radical (21, 25, 29, 32) shows that with an increase in the length of the carbon chain, the kinematic viscosity at 100°C increases from 1.55 to 3.68 mm^2/s, at 40°C – from 3.56 to 11.34 mm^2/s, VI increases from 93 to 247 points, the pour point changes from -50 to -36°C, and the flash point increases from 165 to 200°C. Similar changes are observed in unsymmetrical esters containing an aromatic radical.

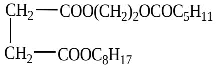
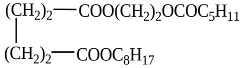
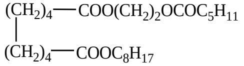
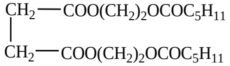
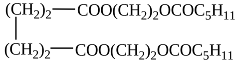
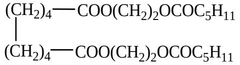
An analysis of viscosity-temperature properties of symmetrical and asymmetrical esters showed that the latter exhibit improved low-temperature characteristics. For example, when one of the cyclic radicals in the molecule of the symmetrical sebacic acid ester (15) is replaced with an aliphatic radical (32), the following changes are observed: the freezing point decreases from -28 to -36°C, the viscosity index (VI) increases from 178 to 247 points, and the flash point increases from 195 to 200°C.

As shown in the data in Table 2, unsymmetrical esters of (C_3–C_{10}) dibasic acids surpass aviation oil *ИПМ-10* and industrial oil И-5-А in terms of VI and flash point. In addition, the pour point of these esters is much lower than that of *И-5-А* oil.

The viscosity-temperature properties of complex esters of (C_3–C_{10}) dicarboxylic acids are presented in Table 3.

Table 3

Viscosity-temperature characteristics of complex esters of (C_3 - C_{10}) dicarboxylic acids

No.	Ester	Kinematic viscosity, mm²/s		VI	Pour point, °C	Flash point, °C
		100°C	40°C			
34	 $\begin{array}{l} CH_2-COO(CH_2)_2OCOC_5H_{11} \\ \vert \\ CH_2-COOC_8H_{17} \end{array}$	1.35	2.91	99	-44	160
35	 $\begin{array}{l} (CH_2)_2-COO(CH_2)_2OCOC_5H_{11} \\ \vert \\ (CH_2)_2-COOC_8H_{17} \end{array}$	1.64	3.18	178	-28	172
36	 $\begin{array}{l} (CH_2)_4-COO(CH_2)_2OCOC_5H_{11} \\ \vert \\ (CH_2)_4-COOC_8H_{17} \end{array}$	2.30	5.92	275	-13	206
37	 $\begin{array}{l} CH_2-COO(CH_2)_2OCOC_5H_{11} \\ \vert \\ CH_2-COO(CH_2)_2OCOC_5H_{11} \end{array}$	1.68	3.95	100	-46	170
38	 $\begin{array}{l} (CH_2)_2-COO(CH_2)_2OCOC_5H_{11} \\ \vert \\ (CH_2)_2-COO(CH_2)_2OCOC_5H_{11} \end{array}$	4.77	19.92	171	-36	190
39	 $\begin{array}{l} (CH_2)_4-COO(CH_2)_2OCOC_5H_{11} \\ \vert \\ (CH_2)_4-COO(CH_2)_2OCOC_5H_{11} \end{array}$	10.22	55.96	173	-28	217
Hydroil HM 10		2.7	8-14	108	-30	160
Industrial oil И-3-А		-	3-3.5	-	≤-18	≥90

The obtained data indicate that in complex esters containing three ester groups (34, 35, 36), with an increase in the length of the carbon chain in the acid fragment, the kinematic viscosity at 100°C increases from 1.35 to 2.30 mm²/s, at 40°C - from 2.91 to 5.92 mm²/s. The viscosity index increases from 99 to 275 points, the pour point rises from -44 to -13°C, and the flash point increases from 160 to 206°C. Similar changes are observed in complex esters containing four ester groups.

The synthesized esters are low-viscosity compounds and possess characteristics that make them suitable for use as bases for instrument, hydraulic, and industrial oils, low-viscosity aviation oils, working and cutting fluids, such as *РЖ-8, AVISTA HYD HLP 10, Hydroil HM 10, И-3-А, И-5-А*.

Study of viscosity-temperature characteristics of compositions based on dicarboxylic acid esters and mineral oils

The preparation of compositions based on esters and mineral oils was carried out at room temperature due to good solubility of esters in mineral oils. 10% compositions based on synthesized esters of (C_3-C_{10}) dicarboxylic acids with mineral oils T-46 and AK-15 were obtained. The viscosity-temperature properties of the obtained compositions were studied. The data are given in Tables 4 and 5.

Addition of esters of (C_3-C_{10}) dicarboxylic acids to T-46 oil improves its viscosity-temperature characteristics. In particular, VI increases from 60 to 86, flash point - from 195 to 228°C. In addition, most compositions are characterized by a decrease in the pour point compared to the base oil (from -10 to -44°C), which indicates improved low-temperature properties.

Table 4

Viscosity-temperature properties of compositions based on esters of (C_3-C_{10}) dicarboxylic acids and mineral oil T-46

No.	Composition	Kinematic viscosity, mm²/s		d_4^{20}	VI	Pour point, °C	Flash point, °C
		100⁰C	40⁰C				
T-46 oil		8.61	81.33	0.900	60	-10	195
1	T-46+10% ester (21)	5.96	42.5	0.904	77	-33	210
2	T-46+10% ester (25)	6.44	48.8	0.909	73	-36	218
3	T-46+10% ester (29)	6.66	51.8	0.910	73	-40	220
4	T-46+10% ester (32)	6.75	53.2	0.908	72	-44	222
5	T-46+10% ester (19)	4.59	26.3	0.905	80	-30	208
6	T-46+10% ester (24)	5.42	36.8	0.905	72	-33	214
7	T-46+10% ester (27)	6.07	42.2	0.908	83	-38	220
8	T-46+10% ester (22)	4.16	24.2	0.904	48	-28	205
9	T-46+10% ester (30)	5.02	30.5	0.906	85	-37	223
10	T-46+10% ester (14)	6.65	52.1	0.915	71	-36	225
11	T-46+10% ester (15)	6.98	57.2	0.907	70	-40	228
12	T-46+10% ester (10)	5.52	35.8	0.910	86	-41	224

Table 5

Viscosity-temperature properties of compositions based on esters of (C_3-C_{10}) dicarboxylic acids and mineral oil AK-15

No.	Composition	Kinematic viscosity, mm²/s		VI	Pour point, °C	Flash point, °C
		100°C	40°C			
AK-15 oil		15.9	-	49	-6	205
1	AK-15+10% ester (15)	9.82	67.60	127	-41	215
2	AK-15+10% ester (25)	6.58	50.64	73	-31	200
3	AK-15+10% ester (29)	8.96	64.27	115	-27	215
4	AK-15+10% ester (22)	6.02	36.14	111	-37	195
5	AK-15+10% ester (32)	8.13	54.98	117	-32	213
6	AK-15+10% ester (27)	6.90	44.06	113	-32	211
7	AK-15+10% ester (14)	6.89	55.48	71	-34	213
8	AK-15+10% ester (10)	7.23	45.18	121	-22	212
9	AK-15+10% ester (30)	5.90	37.31	100	-23	195
10	AK-15+10% ester (24)	6.58	42.74	108	-27	207
11	AK-15+10% ester (21)	10.10	72.09	123	-37	210
12	AK-15+10% ester (19)	6.74	46.03	99	-35	206

According to the obtained results, the addition of 10% synthesized esters of (C_3–C_{10}) dicarboxylic acids to the mineral oil AK-15 increases the viscosity index (from 49 to 127) and the flash point (from 205 to 215°C), while significantly lowering the freezing point of the base oil (from -6 to -41°C).

Determination of the thermo-oxidative stability of compositions

An assessment of the thermo-oxidative stability of 5% and 10% compositions based on dibenzyl esters of malonic and adipic acids with turbine oil T-46 was conducted in accordance with the requirements of ГОСТ 11063-2020.

Based on the conducted studies, it was found that all compositions demonstrate high thermo-oxidative stability. The addition of 5% ester content to mineral oil T-46 leads to a significant reduction in the amount of sediment after oxidation, decreasing it from 3.15 to 0.02 wt.%.

Tribological Analysis of Anti-Scuffing and Anti-Wear Properties of Lubricating Compositions

During the study, the lubricating properties of compositions based on synthesized esters and mineral oil AK-15 were examined. The following parameters were evaluated: scuffing index, critical load, welding load, and wear scar diameter. The data are presented in Table 6.

Table 6

Comparative analysis of lubricating properties of compositions based on esters and AK-15 oil

No.	Composition	Scuffing index (S_i), N	Critical load (P_{cr}), N	Welding load (P_c), H	Wear scar diameter (WSD), mm
1	AK-15+10% ester (15)	410	760	950	0.45
2	AK-15+10% ester (25)	429	784	980	0.42
3	AK-15 +10% ester (29)	450	800	970	0.40
4	AK-15+10% ester (22)	330	570	890	0.65
5	AK-15+10% ester (32)	425	770	940	0.47
6	AK-15+10% ester (27)	440	810	960	0.43
7	AK-15+10% ester (14)	460	830	980	0.38
8	AK-15+10% ester (10)	420	740	920	0.50
9	AK-15+10% ester (30)	340	580	880	0.63
10	AK-15+10% ester (24)	410	750	930	0.48
11	AK-15+10% ester (21)	337	588	882	0.60
12	AK-15+10% ester (19)	390	720	910	0.52
DOS		256	500	-	0.69
Pentaerythritol		290	500	-	0.79

The results showed that compositions containing succinates and adipates demonstrated the best anti-wear and antiwelding properties.

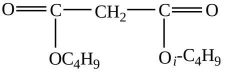
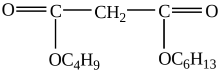
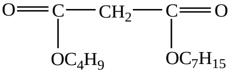
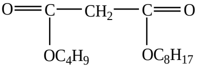
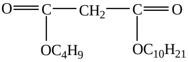
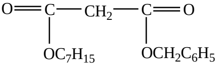
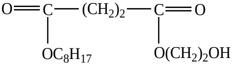
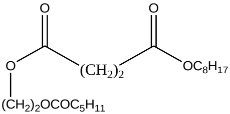
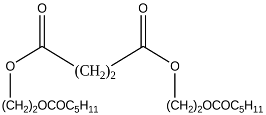
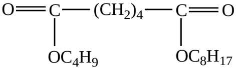
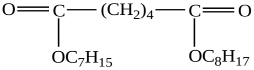
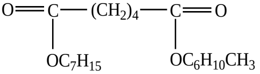
The influence of the structural specificity of complex esters of (C_3-C_{10}) dicarboxylic acids on the thermo-oxidative properties of hydrotreated diesel fuels

The synthesized esters were tested as antioxidant additives to hydrotreated diesel fuel in accordance with ГОСТ 305-2013. The esters were added to the diesel fuel at a concentration of 0.004%.

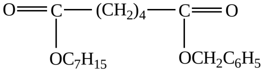
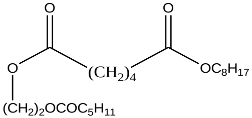
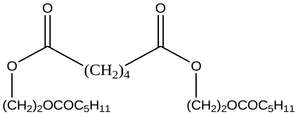
The process was carried out using the “*ЛСАРТ*” apparatus at 120°C for 4 hours in accordance with ГОСТ 9144-79. The results of the study are presented in Table 7.

Table 7

Antioxidant properties of esters of (C_3-C_{10}) dicarboxylic acids

No.	Ester	Amount of sediment, mg/100 ml	
		diesel fuel	diesel fuel with additives
1	2	3	4
16	 $O{=}C(OC_4H_9)-CH_2-C(Oi\text{-}C_4H_9){=}O$	4.3	1.5
17	 $O{=}C(OC_4H_9)-CH_2-C(OC_6H_{13}){=}O$	4.3	2.3
18	 $O{=}C(OC_4H_9)-CH_2-C(OC_7H_{15}){=}O$	4.3	0.6
19	 $O{=}C(OC_4H_9)-CH_2-C(OC_8H_{17}){=}O$	4.3	0.9
20	 $O{=}C(OC_4H_9)-CH_2-C(OC_{10}H_{21}){=}O$	4.3	2.6
22	 $O{=}C(OC_7H_{15})-CH_2-C(OCH_2C_6H_5){=}O$	4.3	1.6
26	 $O{=}C(OC_8H_{17})-(CH_2)_2-C(O(CH_2)_2OH){=}O$	4.0	2.9
34		4.0	2.6
37		4.0	1.9
27	 $O{=}C(OC_4H_9)-(CH_2)_4-C(OC_8H_{17}){=}O$	5.9	0.7
28	 $O{=}C(OC_7H_{15})-(CH_2)_4-C(OC_8H_{17}){=}O$	5.9	0.1
29	 $O{=}C(OC_7H_{15})-(CH_2)_4-C(OC_6H_{10}CH_3){=}O$	5.9	4.2

Continuation of Table 7

1	2	3	4
30	 $O{=}\underset{OC_7H_{15}}{\underset{\vert}{C}}-(CH_2)_4-\underset{OCH_2C_6H_5}{\underset{\vert}{C}}{=}O$	5.9	1.5
35		4.0	1.3
38		5.9	0.3

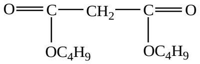
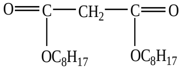
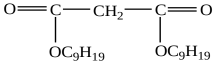
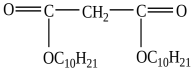
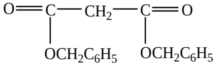
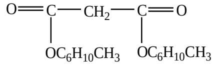
The tests have shown that the best antioxidant properties are demonstrated by unsymmetrical esters of malonic and adipic acids. In particular, butyl-heptyl and butyl-octyl malonates reduce the sediment value from 4.3 to 0.6 mg/100 ml and 0.9 mg/100 ml, respectively, and butyl-octyl and heptyl-octyl adipates reduce it from 5.9 to 0.7 mg/100 ml and 0.1 mg/100 ml, respectively. The most effective among the complex esters is the adipic acid ester (38), which reduces the sediment value from 5.9 to 0.3 mg/100 ml.

Study of esters of (C_3-C_{10}) dicarboxylic acids as components of preservative fluids

Synthesized esters of (C_3-C_{10}) dicarboxylic acids were studied as components of preservation fluids. For this purpose, 3% and 10% compositions with T-30 turbine oil were prepared and tested for corrosion resistance using the "*CORROSIONBOX-1000E*" apparatus (in accordance with ASTM E-85), the "Г-4" hydrochamber, seawater, and 0.001% H_2SO_4 solution. The anticorrosion properties of 3% and 10% compositions of malonic, succinic and adipic acid esters in various aggressive environments were studied. The results are presented in Tables 8 and 9.

Table 8

Results of the study of malonic acid esters as components of preservation fluids

Ester	Concentration of ester in turbine Oil T-30, %	Duration of Corrosion Protection, days		
		Hydrochamber «Г-4»	Seawater	0.001% H_2SO_4 solution
 $O{=}C(OC_4H_9){-}CH_2{-}C(OC_4H_9){=}O$	3	95	81	47
	10	122	103	50
 $O{=}C(OC_8H_{17}){-}CH_2{-}C(OC_8H_{17}){=}O$	3	82	74	42
	10	114	90	46
 $O{=}C(OC_9H_{19}){-}CH_2{-}C(OC_9H_{19}){=}O$	3	85	67	37
	10	117	82	43
 $O{=}C(OC_{10}H_{21}){-}CH_2{-}C(OC_{10}H_{21}){=}O$	3	77	40	35
	10	105	48	39
 $O{=}C(OCH_2C_6H_5){-}CH_2{-}C(OCH_2C_6H_5){=}O$	3	100	89	49
	10	128	116	62
 $O{=}C(OC_6H_{10}CH_3){-}CH_2{-}C(OC_6H_{10}CH_3){=}O$	3	80	70	45
	10	115	90	58
K-17	-	70	70	-
НГ-203А	-	83	16	-

The duration of protection for mineral oil T-30 is 35 days in the hydrochamber, 15 days in seawater, and 9 days in a 0.001% H_2SO_4 solution. In comparison, 10% compositions of malonic acid esters provide protection: from 105 to 128 days in the “Г-4” hydrochamber, from 48 to 116 days in seawater and from 39 to 62 days in the sulfuric acid solution.

The results show that compositions based on monoesters of (C_4-C_{10}) dicarboxylic acids with T-30 turbine oil in the “*CORROSIONBOX-1000*E” apparatus provide a corrosion protection effect of over 300 days, which significantly exceeds the protective characteristics of industrial preservation fluids *K-17* and *НГ-203А* (70 and 83 days, respectively). In seawater and 0.001% H_2SO_4 solution, the best anticorrosive efficiency is exhibited by 3% and 10% compositions based on monoheptyl adipate (102-117 and 91-108 days), monobutyl adipate (110-125 and 97-116 days) and monobutyl succinate (123-130 and 119-122 days, respectively).

Table 9
Results of the study of monoesters of (C_4-C_{10}) dicarboxylic acids as components of preservation fluids

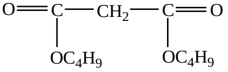
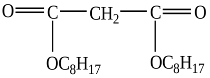
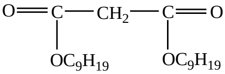
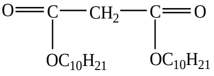
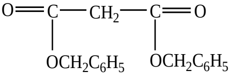
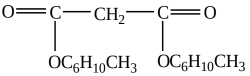
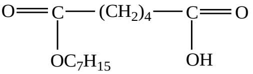
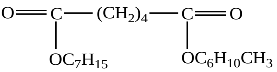
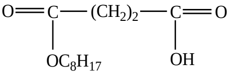
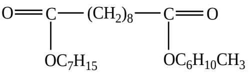
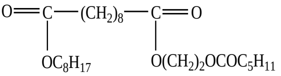
No.	Monoester	Concentration of ester in turbine Oil T-30, %	Duration of Corrosion Protection, days		
			CORROSION BOX-1000E (condensation phase)	Seawater	0.001% H_2SO_4 solution
1	Monobutyl succinate	3	324	123	119
		10	338	130	122
2	Monooctyl succinate	3	330	98	93
		10	338	104	99
3	Monobutyl adipate	3	326	110	97
		10	347	125	116
4	Monoheptyl adipate	3	341	102	91
		10	353	117	108
5	Monooctyl adipate	3	330	92	87
		10	345	96	92
6	Monomethyl-cyclohexyl adipate	3	335	80	73
		10	353	84	79
7	Monobenzyl adipate	3	329	64	59
		10	345	78	70
8	Monooctyl sebacate	3	339	74	70
		10	347	87	82
9	Monomethyl-cyclohexyl sebacate	3	336	59	53
		10	353	64	60
К-17		-	70	70	-
НГ-203А		-	83	16	-

Study of the bactericidal activity of esters of (C_3-C_{10}) dicarboxylic acids

The bactericidal properties of synthesized esters of (C_3-C_{10}) dicarboxylic acids against sulfate-reducing bacteria (SRB) were studied. The results of the study of the bactericidal-inhibitory characteristics of these esters are presented in Table 10.

Table 10

Results of the study of bactericidal properties of esters of (C_3-C_{10}) dicarboxylic acids

No.	Ester	Compound concentration, mg/l	Bacterial count (cell count/ml)	Concentration of H_2S, mg/l	Bactericidal effect, Z-%
1	 $O{=}C(OC_4H_9){-}CH_2{-}C(OC_4H_9){=}O$	5	10^1	10.9	97
		25	10^1	1.5	99.6
		50	-	-	100
2	 $O{=}C(OC_8H_{17}){-}CH_2{-}C(OC_8H_{17}){=}O$	5	10^1	13.1	96.5
		25	10^1	3.6	99
		50	-	-	100
3	 $O{=}C(OC_9H_{19}){-}CH_2{-}C(OC_9H_{19}){=}O$	5	10^1	19	95
		25	10^1	-	99.6
		50	-	-	100
4	 $O{=}C(OC_{10}H_{21}){-}CH_2{-}C(OC_{10}H_{21}){=}O$	5	10^1	7.5	98
		25	10^1	1.7	99.5
		50	-	-	100
5	 $O{=}C(OCH_2C_6H_5){-}CH_2{-}C(OCH_2C_6H_5){=}O$	5	10^1	10.9	97
		25	10^1	3.6	99.04
		50	-	-	100
6	 $O{=}C(OC_6H_{10}CH_3){-}CH_2{-}C(OC_6H_{10}CH_3){=}O$	5	10^1	33.5	91
		25	10^1	5.5	98.5
		50	-	-	100
7	 $O{=}C(OC_7H_{15}){-}(CH_2)_4{-}C(OH){=}O$	50	-	-	100
		100	-	-	100
		200	-	-	100
8	 $O{=}C(OC_7H_{15}){-}(CH_2)_4{-}C(OC_6H_{10}CH_3){=}O$	50	10^5	171	54.4
		100	10^4	139.8	62.7
		200	10^3	100	73
9	 $O{=}C(OC_8H_{17}){-}(CH_2)_2{-}C(OH){=}O$	50	10^3	96.4	74.2
		100	-	-	100
		200	-	-	100
10	 $O{=}C(OC_7H_{15}){-}(CH_2)_8{-}C(OC_6H_{10}CH_3){=}O$	50	10^2	56.3	85
		100	-	-	100
		200	-	-	100
11	 $O{=}C(OC_8H_{17}){-}(CH_2)_8{-}C(O(CH_2)_2OCOC_5H_{11}){=}O$	50	-	-	100
		100	-	-	100
		200	-	-	100

The obtained data indicate the high bactericidal properties of malonic acid diesters against sulfate-reducing bacteria. At a concentration of 5 mg/l, symmetrical esters of malonic acid (MA) exhibit over 90% bactericidal efficacy, and at 50 mg/l, they completely inhibit bacterial growth, providing 100% protection. In comparison, industrial inhibitors *АМДОР-ИК-7* and *АМДОР-ИК-10*, at the same concentration (50 mg/l), show only 60% and 40% biocidal efficacy, respectively. The impact of symmetric MA esters on SRB viability is also illustrated in the diagram (Fig. 9).

The monoheptyl ester of adipic acid and the complex ester of sebacic acid demonstrate high efficiency, providing 100% inhibition of SRB growth at all tested concentrations.

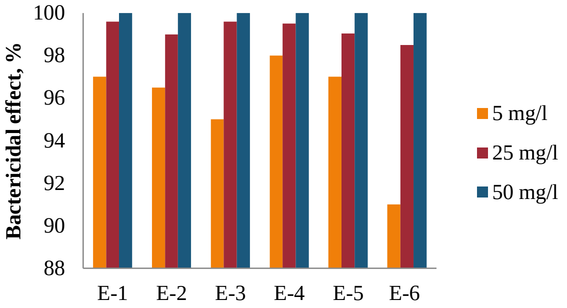


Fig. 9. Bactericidal activity of malonic acid esters

The monoester of succinic acid and the unsymmetrical ester of sebacic acid at concentrations of 100 and 200 mg/l also demonstrate complete inhibition of bacterial cell growth.

Study of the plasticizing characteristics of diesters of (C_3-C_{10}) dicarboxylic acids

Synthesized esters of (C_3-C_{10}) dicarboxylic acids were used as plasticizers for polymer matrices such as high-density polyethylene (HDPE), polypropylene (PP), and polyvinyl chloride (PVC). The plasticizing properties of the obtained polymeric materials were studied, and the results are presented in Tables 11 and 12.

In HDPE, the sample containing dioctyl malonate exhibited the highest tensile strength (30.06 MPa). In PP, three plasticizers provided high values of tensile strength (30.75, 28.47, and 29.88

MPa) and elongation at break (850%, 870%, and 930%). For PVC, the sample with dioctyl malonate demonstrated the highest tensile strength, reaching 36.52 MPa.

Table 11

Mechanical properties of plasticizing compositions

No.	Composition, wt. %	Tensile stress at break, MPa	Elongation at break, %
1	100% HDPE	22.95	19
2	HDPE + 1% P_1	30.06	19
3	HDPE + 1% P_2	21.79	10
4	HDPE + 1% P_3	24.43	12
5	100% PP	24.28	437
6	PP + 1% P_1	30.75	850
7	PP + 1% P_2	29.88	930
8	PP + 1% P_3	28.47	870
9	PVC + 1% P_1	36.52	52
10	PVC + 1% P_2	34.36	57

*P_1 – dioctyl malonate, P_2 – 4-methylcyclohexyl-heptyl malonate, P_3 – benzyl-heptyl malonate.

Table 12

Mechanical properties of plasticizing compositions

No.	Composition, wt. %	Ultimate tensile strength, MPa	Elongation at break, %
1	2	3	4
1	100% HDPE	30.0	32
2	HDPE + 1% P_4	21.2	12
3	HDPE + 1% P_5	28.5	18
4	HDPE + 1% P_6	30.2	20

Continuation of Table 12

1	2	3	4
5	HDPE + 1% P_7	32.0	20
6	100% PP	34.0	970
7	PP + 1% P_4	35.1	1000
8	PP + 1% P_5	34.3	980
9	PP + 1% P_6	32.0	960
10	PP + 1% P_7	30.3	880
11	100% PVC	30.8	16
12	PVC + 20% P_7	15.6	34

*P_4 – di(4-methylcyclohexyl)adipate, P_5 – di(4-methylcyclohexyl)sebacate, P_6 – 4-methylcyclohexyl-heptyl adipate, P_7 – 4-methylcyclohexyl-heptyl sebacate.

The physico-mechanical properties of compositions based on symmetric and asymmetric esters of adipic and sebacic acids indicate an ambiguous effect of additives on the plasticizing properties of polymers. The addition of 1 wt.% of the unsymmetrical ester (4-methylcyclohexyl-heptyl ester) increases the tensile strength of HDPE, while the symmetric diester of adipic and sebacic acids provides the best values of tensile strength and elongation at break for PP (35.1 MPa and 34.3 MPa, 1000% and 980%, respectively). It was found that adding 20 wt.% of the 4-methylcyclohexyl-heptyl sebacate to PVC increases the elongation at break of the composite.

Development of a technology for producing an unsymmetrical ester of (C_3-C_{10}) dicarboxylic acids

A process flow diagram was developed for the esterification reaction, using the synthesis of an unsymmetrical malonic acid ester as an example. The technological process for obtaining an unsymmetrical diester involves two main stages (Fig. 10): the synthesis of a monoester followed by its esterification to the corresponding diester.

The stages are carried out sequentially in a reactor (7) equipped with a mechanical stirrer. The starting reagents – malonic acid, 1-butanol, and a solvent (p-xylene) are fed from storage tanks (1, 2, and 3) via lines I, II, and III into a mixer (4), where they are pre-mixed. The resulting mixture is then pumped via line IV into the top of the reactor (7) using a pump (5). Simultaneously, the catalyst (KU-2-8) is introduced into the reactor through line V. After the reagents are loaded, electric heating and stirring are initiated. The esterification process is conducted under continuous stirring for 4 hours, maintaining the reactor temperature within the range of 130–135°C. The reaction proceeds until the complete removal of water from the reaction mixture by azeotropic distillation with p-xylene. The reaction mixture is then cooled to 50°C in a heat exchanger (8) and directed via line VI to a filtration unit (9), where mechanical impurities and catalyst particles are removed. The liquid phase containing the azeotropic water–p-xylene mixture flows through line VII into an atmospheric distillation column (10), where phase separation occurs: water is withdrawn from the top of the column and sent to the water treatment system, while p-xylene is returned to the process (tank 3) for reuse.

At the second stage, *n*-octanol is introduced into the reactor (7) containing the monoester via line IV from tank (6). The esterification continues at 130–135°C until the calculated amount of reaction water is removed and the acid number of the esterification product reaches 6 mg KOH/g.

The final product is purified by fractional distillation in a vacuum distillation column (11) under a residual pressure of 20 mm Hg and a temperature of 345°C. The reaction mixture is fed to the column via line VIII. The purified esterification product is cooled in a heat exchanger (12) via line IX, and then distributed via lines X and XI into tanks (13 and 14), where the products – monoester and diester are separated.

The distillation residue, a resinous liquid by-product, is discharged through the bottom drain valve of the reactor.

The obtained product – monoester (a by-product) and the unsymmetrical diester are transported to the finished product storage area for further use or storage. The monoester can be reintroduced into the reactor for further esterification or used as a bactericidal inhibitor and a component in preservation fluids.

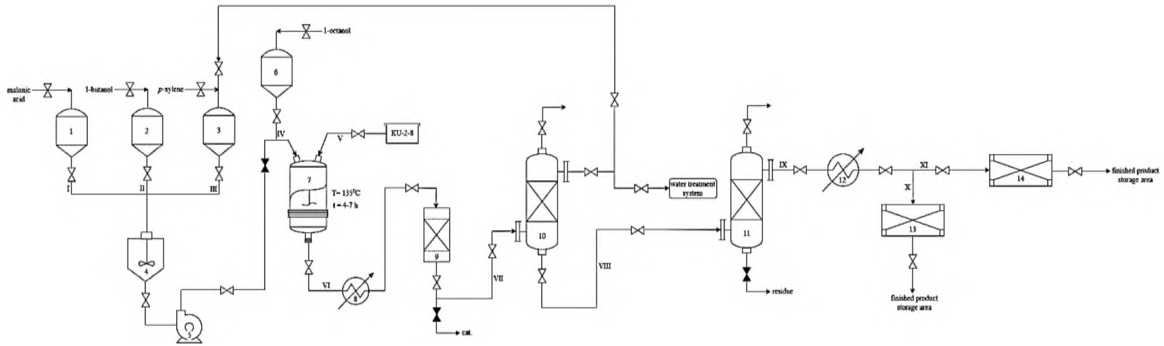


Fig. 10. Developed technological scheme for the production of malonic acid ester

1 – tank for malonic acid; 2 – tank for butanol-1; 3 – tank for *p*-xylene; 4 – mixer; 5 – pump; 6 – tank for octanol-1; 7 – reactor with a stirrer and heating, 8, 12 – heat exchangers, 9 – filtration unit; 10 – atmospheric distillation column; 11 – vacuum distillation column; 13, 14 – product storage tanks

CONCLUSIONS

1. Symmetrical and asymmetrical diesters, as well as complex esters of malonic, succinic, adipic, and sebacic acids were synthesized using KU-2-8 and Tseokar-2 catalysts in a p-xylene medium. The product yields ranged from 70% to 90%, with selectivity of 75% to 91%. The viscosity-temperature properties of the esters were studied. These esters can be recommended as a base for low-viscosity synthetic oils, such as *РЖ-8, ИПМ-10, И-3-А*, *И-5-А*, *Hydroil HM 10*, *Avista HYD HLP 10* [1-2, 4, 8-9, 14, 18, 20, 23].
2. The synthesized mono- and diesters were investigated as components of preservation fluids and demonstrated high protective properties against corrosion. The anticorrosive efficiency of 3 and 10% compositions prepared on the basis of monoesters with T-30 mineral oil was as follows: 324 – 353 days in the “*CORROSIONBOX-1000E*” apparatus, 59 – 130 days in seawater, and 53 – 122 days in a 0.001% sulfuric acid solution [12, 13].
3. Symmetrical esters of malonic acid were tested for the first time as bactericidal inhibitors and demonstrated a high protective effect against sulfate-reducing bacteria (SRB) at low concentrations (5, 25 and 50 mg/l). It was found that at a concentration of 5 mg/l, they exhibited a bactericidal effect of 91–98%, while at 50 mg/l they completely inhibited bacterial cell growth. Monoheptyl adipate and monooctyl succinate were also evaluated for bactericidal activity and demonstrated a 100% bactericidal effect at 50 mg/l [21, 25, 26, 28].
4. Unsymmetrical malonic acid esters were tested for the first time as antioxidant additives for hydrotreated diesel fuel. It was found that butyl-heptyl and butyl-octyl esters of malonic acid reduce the amount of sediment from 4.3 mg/100 ml to 0.6 and 0.9 mg/100 ml, respectively. Unsymmetrical and complex esters of adipic acid also demonstrated high antioxidant properties. Thus, a complex ester, as well as heptyl-octyl, butyl-octyl, and benzyl-heptyl esters of adipic acid, reduce the amount of sediment from

5.9 mg/100 ml to 0.3, 0.1, 0.7, and 1.5 mg/100 ml, respectively [3, 5, 7, 22].

5. Symmetrical and unsymmetrical esters of malonic, adipic and sebacic acids were tested as plasticizers for polypropylene, polyvinyl chloride, and high-density polyethylene. It was found that samples containing octyl, methylcyclohexyl-heptyl and benzyl-heptyl diesters of malonic acid demonstrate high values for tensile strength at break (30.75, 29.88, and 28.47 MPa) and elongation at break (850, 930, and 870%, respectively). Composites based on dimethylcyclohexyl esters of adipic and sebacic acids with polypropylene also have high ultimate tensile strength (35.1 and 34.3 MPa, respectively) and elongation at break (1000 and 980%, respectively) [15, 16, 19].
6. The thermo-oxidative and thermal stability of the synthesized esters was studied. It was found that in 5% compositions based on dibenzyl esters of adipic and sebacic acids with T-46 mineral oil, the amount of sediment after oxidation decreases from 3.15 to 0.01 wt.%. Thermal analysis of esters of (C_3-C_{10}) dicarboxylic acids showed that the highest thermal stability is exhibited by unsymmetrical esters of adipic acids (269–370°C) and the symmetrical ester of sebacic acid (323–396°C) [24].
7. The lubricating properties of compositions prepared on the basis of synthesized esters and mineral oil AK-15 were studied and it was found that compositions with succinates and adipates exhibit the best anti-wear (WSD = 0.42 mm and WSD = 0.38 mm, respectively) and antiwelding (S_i = 429 N and S_i = 460 N, P_{cr} = 784 N and P_{cr} = 830 N, respectively) characteristics. These indicators significantly exceed the results of industrial oils, such as DOS and pentaerythritol.
8. A technological scheme for the production of esters of (C_3-C_{10}) dicarboxylic acids was developed, using unsymmetrical malonic acid ester as an example.

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