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ABSTRACT

of the dissertation for the degree of
Doctor of Philosophy

SYNTHESIS AND STUDY OF SYNTHETIC PETROLEUM ACIDS MIXTURE IN CATALYTIC PRESENCE OF ACETYLACETONE COMPLEXES WITH TRANSITION METALS (Co, Cr, Ni, Mn, Zn)

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The work was performed at laboratory of "Liquid-phase oxidation" of academician Y.H. Mammadaliyev Institute of Petrochemical Processes of Azerbaijan National Academy of Sciences

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GENERAL CHARACTERISTICS OF THE WORK

The relevance of the work. Currently, one of the main requirements of local economy is increasing petroleum-based organic acid resources due to the expansion of their application fields[1]. Petroleums consist very small amount of organic acids and their composition vary in a wide range. Earlier, the Heydar Aliyev Oil Refinery produced a mixture of natural petroleum acids from both kerosene and diesel distillates. Currently, diesel distillate is hydropurified without acid removal and acid is converted into a suitable alcohol and remains in diesel fuel. Therefore, the amount of natural petroleum acids that can be used as raw materials in a number of chemical processes sharply reduces. On the other hand, although there is a technology for obtaining saturated fatty acids, many physical and chemical properties (including freezing point and solubility) of the products on their bases don't meet the requirements for them.

Besides, natural petroleum acids - based products were confirmed as competitive products in academician Y.H.Mammad-aliyev Institute of Petrochemical Processes of ANAS. Thus, the Caspian-X inhibitor, created in 1995 for the initial refining of oil, catalytic cracking, catalytic reforming, corrosion protection of coking facilities, is successfully used at the Heydar Aliyev Oil Refinery, and its main raw materials are natural petroleum acids. This inhibitor has no analogue in the world and is the only inhibitor that can be applied without a neutralizer. At the same time, on the basis of natural petroleum acids, a foaming agent for firefighting was created that can be used in sea, river and lake waters.

The reduction of natural petroleum acids reserves and a simultaneous increase in demand for them create a challenge of obtaining synthetic analogues of these acids. The work to be performed should result in the development of new catalytic compounds and technologies for the production of a mixture of synthetic organic acids and their various water-soluble derivatives

[1] Abbasov, V.M. Chemistry of oxygenated organic compounds / V.M.Abbasov, F.A.Nasirov, L.M. Afandiyeva, N.Sh.Rzayeva. Baku: Muallim, -2020. -412 p.

based on diesel distillate of Baku petroleum mixture rich in naphthenic hydrocarbons.

Although a series of works have been carried out in this area, there are still serious problems in the production of high-yield mixtures of synthetic acids and selection of catalysts with high activity. To solve these problems, a process should be developed in such a way that virtually no by-products are obtained by the synthesis of the target products. On the other hand, non-oxidized part of oxidized fraction must be recirculated and used until complete oxidation.

The presented dissertation is devoted to the solution of the above-mentioned problems.

The object and subject of the research. The object of the research is the synthesis of a mixture of synthetic petroleum and oxyacids (SPA+OPA) by liquid phase aerobic oxidation of naphthene-paraffinic hydrocarbons of naphthene-based mixed oils of Azerbaijan. But the subject of the research is to determine the possibility of efficient use of the synthesized synthetic acids mixture.

The purpose and objectives of the research. Obtaining a mixture of high-yield synthetic organic acids by liquid phase catalytic oxidation of dearomatized diesel fraction of mixed oils, synthesis of new catalytic compounds for this purpose, identification of substances obtained by modern research methods and creation of special-purpose competitive reagents based on synthesized acids.

The following studies were conducted for the purpose of achieving the goal:

- ✓ dearomatization of diesel fraction for oxidation process and study of the structural group composition of the obtained naphthene-paraffinic hydrocarbons;
- ✓ study of oxidation process of naphthene-paraffinic hydrocarbons by atmospheric oxygen in the presence of chelate complexes of acetylacetone with variable valence metals and their mixture in different ratios;
- ✓ study of oxidation process in the presence of napthene-paraffinic hydrocarbons with Cr-, Co-, Mn-, Ni-, Zn acetylacetonates and their 2,4-dinitrophenylhydrazine complexes in different ratios;

- ✓ study of the complete oxidation process by recirculation of the non-soapy part (non-oxidized part) obtained by the oxidation process
- ✓ determination of particle size of catalysts in liquid phase of a catalytic system;
- ✓ obtaining esters of a mixture of synthesized synthetic acids and testing them as antioxidants for diesel fuel and effective plasticizers for polyvinyl chloride (PVC);
- ✓ study of the synthesis of synthetic petroleum- and oxyacids nitrogeneous derivatives and their bactericidal properties.

Investigation methods. The studies on the submitted dissertation were conducted in accordance with modern methods and standards. The synthesis of a mixture of synthetic petroleum acids was carried out on a bubbler device. The acid number of the obtained acids was determined in accordance with GOST 5985-79. The structure and composition of diesel fraction and naphthene-paraffinic hydrocarbons, as well as synthesized acids and their derivatives taken as raw materials in the oxidation process, were confirmed by modern spectroscopic methods - IR, ^{1}H NMR, UV. Thermal analysis, X-ray phase analysis, SEM microscope were used in the study of the catalysts structure along with IR spectroscopy. The method of dynamic light scattering was used to measure the particles of the catalyst.

The main provisions submitted to the defense. Aerobic oxidation processes of naphthene-paraffinic hydrocarbons were studied in the catalytic presence of Cr-, Co, Mn-, Ni-, Zn acetylacetonates, as well as their 2,4-dinitrophenylhydrazine complexes, a high yield mixture of synthetic oxy- and petroleum acids was obtained; mixed esters of synthesized organic acids were obtained and recommended for diesel fuel as effective antioxidants and basic and auxiliary plasticizers for polyvinylchloride. Simultaneously, amidoamines and imidazolines based on a mixture of synthetic acids were proven to have a high bactericidal effect.

Scientific novelty of the investigation.

- Liquid phase oxidation of naphthene-paraffinic hydrocarbons in catalytic presence of acetylacetone complexes with transition metals (Cr, Co, Mn, Ni, Zn) in the presence of atmospheric oxygen was carried out and a mixture of high-yield synthetic petroleum and

oxyacids was obtained;

- it was determined that addition of electron-donor ligands during the oxidation of naphthene-paraffinic hydrocarbons in the presence of complexes of β-diketonates of transition metals with 2,4-dinitrophenylhydrazine promotes high yields of SPA+OPA;
- it was determined that a synergetic effect occurs during the oxidation process in the presence of a mixture of the presented catalysts with different ratios, and the yield of SPA+OPA reaches a maximum (40,6%);
- re-oxidation (recirculation) of the non-soapy part was carried out in the presence of the presented catalysts and the yield of the acid mixture obtained from both stages was twice as high (~79%);
- time dependence of catalytic oxidation process of naphthene-paraffinic hydrocarbons in the presence of the catalytic components was studied by spectroscopic method;
- mixed esters based on synthetic petroleum acids and various alcohols were synthesized and studied as effective antioxidants and plasticizers;
- amidoamines and imidazolines were synthesized on the basis of a mixture of synthetic acids and polyethylene polyamine, their complexes with organic and inorganic acids were developed and bactericidal properties were studied. Complexes of amidoamines with inorganic acids were found to have a higher bactericidal effect (93-96%);
- metal salts of a mixture of synthetic acids were tested as additives to conservative fluids and high results were obtained.

Theoretical and practical value of the work. The esters based on a mixture of synthetic acids can be recommended for use in diesel fuel (DF) as effective antioxidants, basic and auxiliary plasticizers. Thus, it was observed that addition of synthesized mixed diesters to 100 ml of diesel fuel (DF) at a concentration of 0,004% reduced sediment amount from 6,0 mg/100 cm^3 to 0,00.

This once again confirms the possibility of using mixed diesters as effective antioxidants. Amidoamine based on SPA+OPA and

polyethylene polyamine (PEPA) and its complexes with inorganic acids can be recommended for use as highly effective inhibitor-bactericide in the field of biocorrosion. Thus, the complexes of synthesized amidoamine with HBr and HNO_3 acids possess 93 and 92,8% of bactericidal effect at a concentration of 125 mg/l respectively, and 96,4 and 96,1% at a concentration of 250 mg/l.

Personal participation of the author. The author outlines the main goals and tasks to achieve them. Problem statement, experiments and tests, systematization and generalization of the results, collection of literature, writing and compiling articles, abstracts and the dissertation were performed by the direct participation of the author.

Approbation of the work. 24 scientific works were published on the topic of the dissertation, including 13 papers and 11 abstracts.

The results of the dissertation work were presented and discussed in the following conferences: International Scientific Conference "Actual Problems of Contemporary Natural and Economic Sciences" dedicated to the 95th anniversary of national leader Heydar Aliyev (Ganja, 2018, 2019), International Scientific-Practical Conference "Innovative Perspectives for the Development of Oil Refining and Petrochemistry" (Baku, 2018 - 2 abstracts), International Chemistry Conference (Turkey, Istanbul, 2019), International Scientific Conference "Actual Problems of Modern Chemistry" (Baku, 2019), International Conference "Technical Thermodynamics: Thermophysical Properties and Energy Systems" (Germany, Rostock, 2020).

The dissertation work was performed at the laboratory of "Liquid phase oxidation" at academician Y.H.Mammadaliyev Institute of Petrochemical Processes of Azerbaijan National Academy of Sciences.

The structure and scope of the work. The dissertation consists of 174 pages including introduction (11523 characters), 5 chapters (the I chapter - 74247 characters, the II chapter - 25219 characters, the III chapter - 38455 characters, the IV chapter - 20773 characters, the V chapter - 21832 characters), conclusions (3808 characters), 187 references, abbreviations. The total volume of the dissertation is 195857 characters (excluding figures, tables, graphs, appendices and list of a cited scientific literature). Dissertation includes 39 tables and 47 figures.

The introduction provides brief information on the relevance

of the topic, scientific novelty, goals and objectives of the research, practical significance, and approbation of the work, research methods, structure and scope.

The first chapter provides the literature review that presents an extensive analysis of the oxidation process of saturated and unsaturated aliphatic and alicyclic hydrocarbons in the presence of atmospheric oxygen and hydrogen peroxide using homogeneous and heterogeneous catalysts, applications of organic acids and their derivatives obtained by the process.

The second chapter describes the methodology of experiments: study of structural-group composition of raw materials and synthesized substances, determination of physical and chemical parameters, synthesis of used catalysts, study of their composition using modern spectroscopic devices.

The third chapter studies liquid phase aerobic oxidation of naphthene-paraffinic hydrocarbons obtained by dearomatization of diesel fraction in the presence of various catalytic compounds. Complexes of acetylacetonates with transition metals and their mixtures in different ratios, as well as 2,4-dinitrophenyl hydrazine complexes of acetylacetonates were used as catalysts in the oxidation process. The present chapter studies physical and chemical properties of the acids obtained as a result of oxidation process, structural-group composition, mechanism of the process, factors influencing the target product yield and the process selectivity.

The fourth chapter describes determination of the optimal parameters of the oxidation process, spectroscopic study of the time dependence of the oxidation process and determination of the particle size of the catalysts.

The fifth chapter is devoted to the study of the synthesis and properties of mixed esters based on synthetic organic acids and various alcohols. SPA- and OPA-based amidoamines and imidazolines were synthesized, their complexes with organic and inorganic acids were developed and inhibitory-bactericidal properties were studied in the chapter.

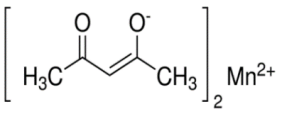
The conclusions, list of cited references, appendices, list of abbreviations are given at the end of the dissertation.

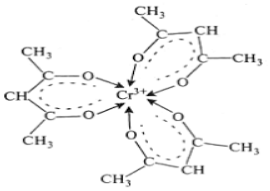
THE MAIN CONTENT OF THE WORK

Fraction of Azerbaijani oils mixture taken from the Heydar Aliyev Baku Oil Refinery, boiling at 185-329°C, was used as a raw material for the implementation of the oxidation process in the presented work. The diesel fraction was purified from aromatic hydrocarbons prior to the oxidation process. Dearomatization process was carried out by sulfonation method. After dearomatization process, the residual content of aromatic hydrocarbons in the fraction was ~2-3%. Physical and chemical properties of the fractions were determined before and after dearomatization process, the structural-group composition was confirmed by spectroscopic analysis methods.

Study of the oxidation process of naphthene-paraffinic hydrocarbons separated from the mixture of Azerbaijani oils in the presence of acetylacetone and chelate complexes with transition metals

Oxidation process of naphthene-paraffinic hydrocarbons was carried out in a bubble-type reactor in the temperature range of 135-140°C, with an air flow rate of 300 *l*/kg·h and a reaction time of 5-7 h. Metal acetylacetonates tested as catalysts in the oxidation process were synthesized[2] by the methods known from literature and their structural properties were determined using modern spectroscopic devices. The chemical structure of Mn- and Cr-acetylacetonates can be presented as follows:





[2] Saeed, M. Synthesis and chemical charaterization of metals (Al, Cr, Co, Mn and VO) complexes with acetylacetone (**β**- diketone) / M.Saeed, Z.Khalid, R.Saleem // Journal of Natural Sciences Research, -2017. V.7, No.19, -p. 49-57

X-ray phase analyses of acetylacetonates of transition metals were carried out in the presence of PANanalytical EMPYREAN X-ray analyzer, and thermal analyses were carried out on LINSEIS STA PT1600 thermogravimetric analyzer (Fig.1, 2).

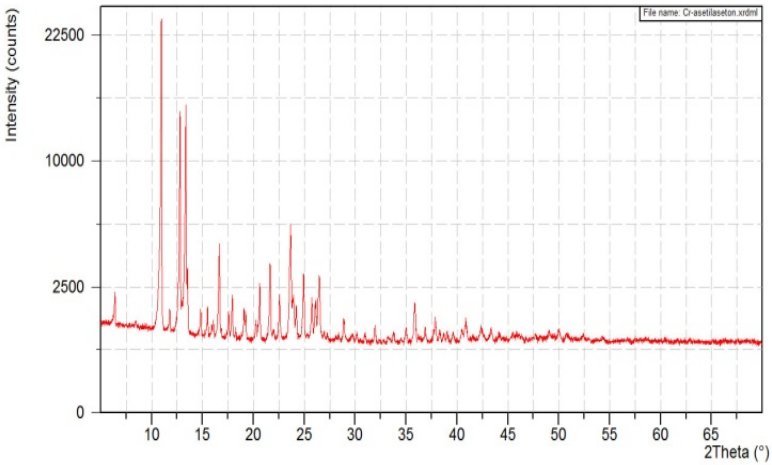


Fig.1. X-ray phase spectrum of $Cr(acac)_3$

According to Fig.1, the main part of the compound $Cr(acac)_3$ is Cr(III) of a monoclinic structure. Cr(III) was observed at 2θ = 11°, 13°, 14°, 16°, 21°, 23°, 24°, 25°, 26°, 28°, 35°, respectively.

According to the analysis of the thermogram of $Mn(acac)_2$, it can be concluded that, a three-stage decomposition of the initial weight of 16,1 mg occurs during heating from 20°C to 1000°C. 1) The mass loss of this compound is ~20,14% that means 0,32 mg of total weight in the temperature range of 60-160°C. 2) The mass loss is up to 22,49% (0,362 mg of total weight) in the temperature range of 160-240°C. 3) The mass loss is 36,18% (0,58 mg of total weight) in the temperature range of 240-400°C. Complete decomposition of the compound occurs in the temperature range of 400-1000°C.

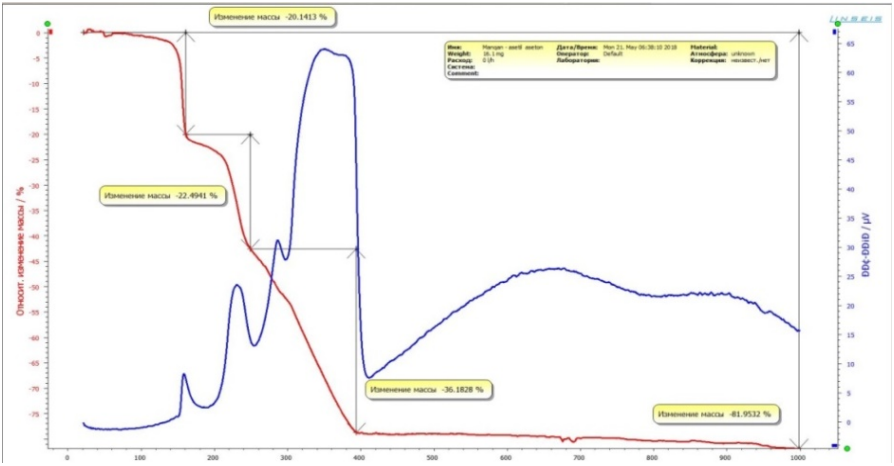


Fig. 2. Spectrum of $Mn(acac)_2$ thermal analysis

The calculated amount of catalyst relative to the raw material was dissolved in a mixture of naphthene-paraffinic hydrocarbons with a known weight and added to a bubbler device, after which the device was equipped with air and heating system and the oxidation process began.

Liquid phase aerobic oxidation process at different concentrations of Me-acetylacetonates ($Me(acac)_n$) was studied and the results was set into Tab. 1.

As is evident from Tab.1, the catalysts possess different activity, which can be explained by their structural characteristics and the number of donor centers. Considering the effect of Cr-Zn salts on the oxidation process, it appears that catalytic effect of Mn-salt taken in the range of 0,1-0,3% mas. is higher than other complexes. Thus, the yield of SPA+OPA in the presence of Mn-salt is on average 26.1%; but it's 17.9% for Cr-salt.

Table 1. Results of oxidation process of naphthene-paraffinic hydrocarbons in the presence of $Me(acac)_n$ (t=135-140°C, air flow rate is 300 *l*/kg·h, reaction time 5 h)

Cat. amount, mas., %	Oxidate		SPA		OPA		SPA+OPA
	Acid number, mgKOH/g	Yield, %	Acid number, mgKOH/g	Yield, %	Acid number, mgKOH/g	Yield, %	Yield, %
Chromium acetylacetonate							
0,1	39	93	125,8	10,3	118,5	5	15,3
0,2	42	94	138,2	12,5	125,2	6,8	19,3
0,3	30	93,5	130,2	10	115,8	9,2	19,2
Manganese acetylacetonate							
0,1	42,3	94,2	138,7	12,8	120,2	8,5	21,3
0,2	52	96,2	146	14	125,2	10	24
0,3	60	96	144,5	13,5	122,6	19,5	33
Cobalt acetylacetonate							
0.1	38,5	95	135,2	11	119,8	8	19
0.2	52,5	95,8	142,2	13,8	124	6,5	20,3
0.3	53,4	95,4	140,8	13,5	124,6	8,6	22,1
Nickel acetylacetonate							
0.1	36,2	95,4	136	8,2	115,4	9	17,2
0.2	50,5	96	140,5	11	122,4	7	18
0.3	50,6	95,4	138,8	10,2	125,2	8,5	18,7
Zinc acetylacetonate							
0.1	25	96	135,2	6,8	110,2	8,5	15,3
0.2	28,8	95,9	138	10,5	115,8	8,8	19,3
0.3	30	96,2	138,5	9	118	9,5	18,5

The reaction proceeds by a radical chain mechanism in the presence of $Me(acac)_n$. The reaction mechanism for the oxidation process in the presence of $Mn(acac)_2$ can be described as follows:

$$Mn^{2+} + O_2 \rightarrow (^{\cdot -}O\text{-}O)Mn^{3+}$$
$$(^{\cdot -}O\text{-}O)\text{-}Mn^{3+} + RH \rightarrow (HOO)\,Mn^{3+} + {}^{\cdot}R$$
$$(HOO)Mn^{3+} + {}^{\cdot}R \rightarrow RO^{\cdot} + {}^{\cdot}OH + Mn^{2+}$$

Simultaneously with the decomposition of hydroperoxides in the presence of a catalyst, the interaction of the catalyst with initial materials can also play a major role (activation of oxygen and

hydrocarbons). Oxygen activation plays a key role in the formation of the oxidation chain (in the presence of a catalyst):

$$Mn^{2+} + O_2 \rightarrow Mn^{2+}\cdots\cdots O_2$$
$$Mn^{2+} \cdots\cdots O_2 + RH \rightarrow Mn^{2+} + R^{\cdot} + HO_2^{\cdot}$$

Liquid phase aerobic oxidation process of naphthene-paraffinic hydrocarbons was carried out in the presence of a mixture of different ratios of Mn- and Cr-acetylacetonates with higher catalytic activity and the results were set into Tab. 2.

Table 2. Results of oxidation process of naphthene-paraffinic concentrate in the presence of a mixture of Cr and Mn acetylacetonates in different ratios (amount of catalyst relative to the raw material 0,2% (mas.), reaction time 5 h)

Catalyst	Oxidate, acid number mgKOH/g	SPA			OPA	
		Yield, %	Acid number /ester number mgKOH/g		Yield, %	Acid number, mgKOH/g
$Cr(acac)_3$:Mn $(acac)_2$= 1:1	60,2	10,8	147,6	22,8	16	118,6
$Cr(acac)_3$:Mn $(acac)_2$= 2:1	61,1	11,1	151,2	23,4	15,8	116,4
$Cr(acac)_3$:Mn $(acac)_2$= 3:1	63,8	15	176	22	20	145,4

As is evident from Tab.2, the combined use of Cr- and Mn complexes leads to an increase in the yield of the obtained acid. The best result was obtained with $Cr(acac)_3$:$Mn(acac)_2$=3:1, and the yield of SPA+OPA was 35%. Generally, a mixture of Cr and Mn acetylacetonates has a synergistic effect, and the yield of acids obtained in this case is even higher than the results obtained when taken separately. Thus, it can be concluded that the third sample can be considered as the most optimal option when the oxidation process

The best result in liquid phase catalytic oxidation of naphthene-paraffinic hydrocarbons is obtained by taking a mixture of catalysts $Cr(acac)_3$:$Mn(acac)_2$=3:1, therefore the dependence of the process on different concentrations and time of the catalyst mixture was studied. The results are set into Tab.3.

Table 3. Results of time dependence of oxidation process of naphthene-paraffinic hydrocarbons in the presence of $Cr(acac)_3$: $Mn(acac)_2$=3:1 (t=135-140°C, air flow rate 300 *l*/kg·h, catalyst concentration according to raw material 0,2% (mas.))

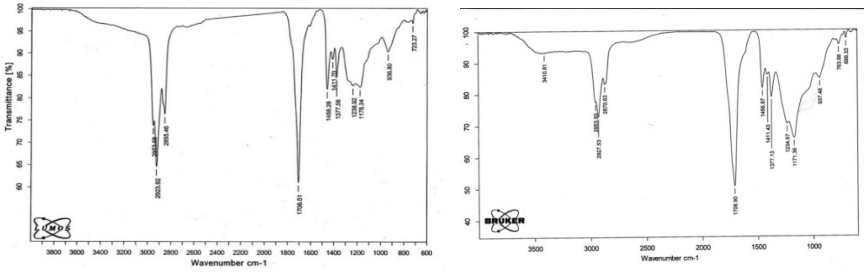
Cat.am. accor.to raw mat., % (mas.)	Oxidate		SPA		OPA		SPA+OPA
	Acid number, mgKOH/g	Yield, %	Acid number, mgKOH/g	Yield, %	Acid number, mgKOH/g	Yield, %	Yield, %
After 5 h							
0,1	58,9	97,7	150	13	148	15	28
0,2	63,8	96	176	15	145,4	20	35
0,3	63,2	96	150,5	15	130,2	18	33
0,4	63	95,6	140,9	14,2	122,6	17,3	31.5
0,5	61,8	95,2	138,5	14	125,8	17,2	31,2
After 6 h							
0,3	64	95,8	145,2	12,2	116,2	16,8	29
0,5	65	95,2	144,5	12	115,7	16,5	28,5

As is evident from Tab. 3, the yield and acid number of obtained acid mixture were higher when the oxidation process was carried out for 5 h. Thus, starting from the 6^{th} h, both the yield and the acid number of the mixture of SPA and OPA obtained during the process begin to decrease. It should be noted that the SPA+OPA mixture obtained during 5h-process has the optimal acid number, yield and molecular weight that is one of the main criteria for the process of obtaining SPA and OPA.

The IR spectra of SPA and OPA obtained by $Cr(acac)_3$:$Mn(acac)_2$=3:1 are presented in Fig. 3.

The following absorption bands are observed according to the IR spectrum of SPA (Fig. 3 (a)): deformation vibrations of C-H bonds of CH_3 and CH_2 groups in the absorption band of 723 cm^{-1}, 1377 cm^{-1}, 1458 cm^{-1} and valence vibrations of C-H bond of these groups in the absorption band of 2855 cm^{-1}, 2923 cm^{-1}, C=O bond of the acid in the absorption band of 1706 cm^{-1}, C-O bond in the absorption band of 1178 cm^{-1}, 1238 cm^{-1}, O-H bond of OH group in the absorption band of 936 cm^{-1}. The values of the absorption bands according to the IR spectrum of OPA were as follows (Fig. 3 (b)): 937, 1708 cm^{-1}

absorption bands belonging to the acid, 1234 cm^{-1} - valence vibrations of C-O bond belonging to the acid, 1171 cm^{-1} - valence vibrations of C-O bonds belonging to alcohol and valence vibrations O-H bond of OH group in 3000-3500 cm^{-1} (3410 cm^{-1} max) belonging to acid and alcohol.



a) b)

Fig. 3. IR spectra of SPA (a) and OPA (b) obtained by $Cr(acac)_3$:$Mn(acac)_2$=3:1

Some physical and chemical properties of SPA obtained by aerobic oxidation process carried out in the presence of $Cr(acac)_3$:$Mn(acac)_2$=3:1 were determined and set into Tab. 4.

Table 4. Physical and chemical properties of SPA obtained by oxidation process

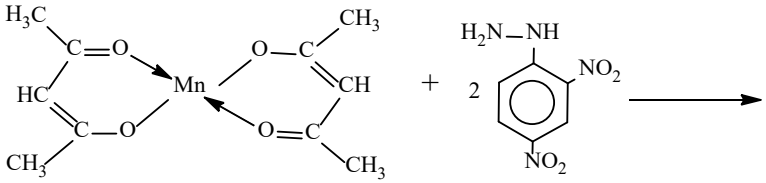
Parameters	SPA
Density, at 20°C ρ_4^{20}, kg/m^3	958,8
Refractive index, n_D^{20}	1,4699
Kinematic viscosity, mm^2/sec (at 50°C)	33,32
Kinematic viscosity, mm^2/sec (at 80°C)	14,00
Sulfonation, % vol.	-
Iodine number, gJ_2/100 g	0,75
Acid number, mg KOH/g	176
Average molecular weight, M_r	318,75
Freezing point, °C	-44,2

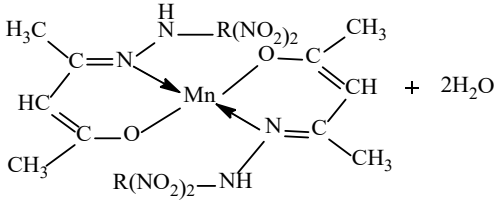
Physical and chemical properties of OPA obtained by oxidation process were also determined: acid number=145,4 mgKOH/g, ρ_4^{20} =1018,2 kg/m^3, $T_{freez.}$ = -19,9°C.

Study of the oxidation process and products of naphthene-paraffinic hydrocarbons in the presence of binary catalytic systems

It is known that addition of electron-donor ligands in the oxidation of naphthene-paraffinic hydrocarbons in the presence of 2,4-dinitrophenylhydrazine complexes of metal-diketonates of transition metals has a positive effect on the yield and selectivity of the process[3]. In addition to $Me(acac)_n$, their 2,4-dinitrophenyl hydrazine (DNPH) derivatives were tested as catalysts to create a stimulating effect on the oxidation of naphthene-paraffinic hydrocarbons.

Complexes of $Me(acac)_n$ with 2,4-dinitrophenylhydrazine were synthesized according to the known method[4]. The reaction equation can be expressed as follows:





Here R – is a phenyl radical.

IR spectrum of the complex of Mn-acetylacetonate with 2,4-DNPH is presented in Fig. 4.

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[3] Aliyeva, L.I. Oxidation of higher linear olefins and some reactions of their conversions / L.I.Aliyeva. – Germany, Lap Lambert Academic Publishing, - 2014. – 176 p.

[4] Novruzova, A.B. Synthesis and crystalline structure of 2,4-pentandion-bis-(2,4-nitrophenylhydrazone) / A.B.Novruzova, M.M.Kurbanova, A.M.Magerramov // Azerbaijan Chemical Journal, - 2010. No 1, - pp. 21-24

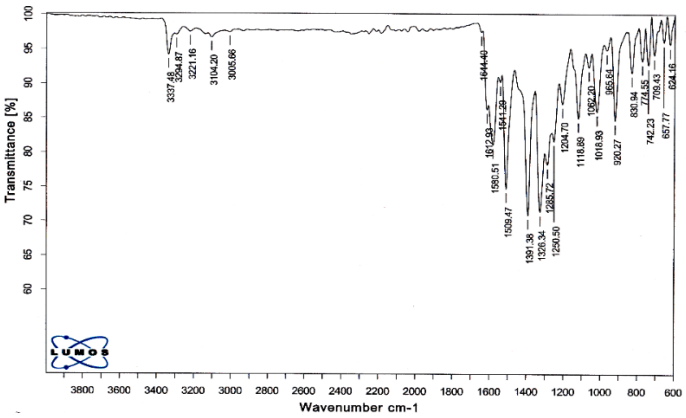


Fig. 4. IR spectrum of 2,4-DNPH complex of Mn(acac)$_2$

Comparing the IR spectra of Mn(acac)$_2$ and 2,4-DNFH complex of Mn(acac)$_2$, it can be concluded that absorption bands of C=N bond appear in the spectrum of the latter at 1580 cm^{-1}. Absorption bands characteristic of symmetrical and asymmetrical vibrations of C-NO$_2$ group occurs at 1509 and 1326 cm^{-1}. In addition, the absorption bands occurring at 1541 and 3221, 3294, 3337 cm^{-1} belong to the deformation and valence vibrations of N-H bond. The absorption bands at 965 and 1644 cm^{-1} can be attributed to the deformation and valence vibrations of C=C bond, respectively. Absorption bands corresponding to C-H bond of the benzene ring are also observed at 709, 742, 830 and 3005 cm^{-1}. Simultaneously, absorption bands corresponding to the C-C bond of the benzene ring appear at 1612 cm^{-1}. 1204, 1250 cm^{-1} shows the absorption bands characteristic for = C-O bond.

The effect of Me(acac)$_n$ 2,4-DNPH complexes on the oxidation of naphthene-paraffinic hydrocarbons was studied (Tab. 5).

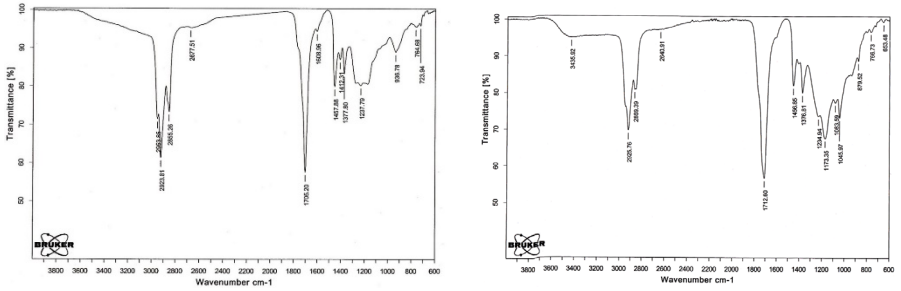
Tab. 5 shows that addition of ligands has different effects on the oxidation process. It should be noted that unlike acetylacetonates, during the oxidation process, the amount of 2,4-DNPH complexes relative to the raw material was 0,2% mas.(the optimal amount of catalyst relative to the raw material is 0,3% in the presence of acetylacetonates,). The highest result among these complexes was

obtained in the presence of 2,4-DNPH complex of $Mn(acac)_2$. Thus, in this case, the yield of synthesized SPA was 18%, and the yield of OPA was 16%.

Table 5. Results of oxidation process of naphthene-paraffinic hydrocarbons in the presence of 2,4-DNPH derivatives of Me-acetylacetonates (catalyst amount for raw material – 0,2% wt., t= 125-130°C, reaction time 5 h)

Catalyst	SPA		OPA		SPA+OPA
	Yield, %	Acid number, mgKOH/g	Yield, %	Acid number, mgKOH/g	Yield, %
The complex of $Mn(acac)_2$ with 2,4-DNPH	18	153	16	143	34
The complex of $Cr(acac)_3$ with 2,4-DNPH	13,2	139,4	10	135,37	23,2
The complex of $Co(acac)_2$ with 2,4-DNPH	15	146,47	11	105	26

IR spectrum of SPA and OPA obtained by the oxidation process of of $Mn(acac)_2$ in the catalytic presence of 2,4-DNPH complex is presented in Fig. 5.



(a) (b)

Fig. 5. IR spectra of SPA (a) and OSA (b) in catalytic presence of 2,4-DNPH complex of $Mn(acac)_2$

The following absorption bands were observed according to the IR spectrum of SPA (Fig. 5 (a)): deformation vibrations of C-H bonds

of CH_3 and CH_2 groups (723 cm^{-1}, 1327 cm^{-1}, 1457 cm^{-1}) and valence vibrations (2855 cm^{-1}), 2923 cm^{-1}, 2953 cm^{-1}); valence vibrations (1705 cm^{-1}) of C=O group belonging to acid; valence vibrations (1237 cm^{-1}) of C-O bond belonging to the acid; valence vibrations (2677 cm^{-1}) of C=O group of acid; deformation vibrations (936 cm^{-1}) of O-H bond of the acid. The following absorption bands were observed according to the IR spectrum of OPA (Fig. 5 (b)): deformation (1376 cm^{-1}, 1411 cm^{-1}, 1456 cm^{-1}) and valence (2869 cm^{-1}, 2925 cm^{-1}) vibrations of CH bonds of CH_3 and CH_2 groups; valence (1712 cm^{-1}) vibrations of C=O group belonging to acid; valence (1173 cm^{-1}, 1234 cm^{-1}) vibrations of C-O bond belonging to the acid; valence vibrations (1170 cm^{-1}) of C-O bond of oxy-groups; deformation vibratrions (940 cm^{-1}) of O-H bond; valence vibrations (3457 cm^{-1}) of O-H bond of the acid. Comparing the IR spectra of SPA and OPA, it can be concluded that the absorption bands of the valence vibrations of C-O bond of acid and oxygroups overlap in the 1170 cm^{-1} band.

Table 6. Results of the oxidation process carried out in the catalytic presence of a mixture of 2,4-DNPH derivatives of acetylacetonates in different ratios (catalyst amount per raw material 0,2% mas.)

Catalyst	SPA		OPA		SPA+ OPA
	Yield,%	Acid number, mgKOH/g	Yield,%	Acid number, mgKOH/g	Yield, %
2,4- DNPH complexes of $Mn(acac)_2$ and $Cr(acac)_3$ (3:1)	15,2	133,6	18,5	120,6	33,7
2,4-DNPH complexes of $Cr(acac)_3$ and $Co(acac)_2$ (3:1)	17,5	147,6	23,1	126,2	40,6
2,4- DNPH complexes of $Mn(acac)_2$ və $Cr(acac)_3$ (1:3)	17	136	19,3	126,5	36,3
2,4-DNPH complexes of $Cr(acac)_3$ and $Co(acac)_2$ (1:3)	16,7	141,5	22	119	38,7

The latter result was obtained as a result of oxidation process in the temperature range of 135-140°C.

Oxidation process was carried out in the presence of a mixture of acetylacetonates with 2,4-dinitrophenyl hydrazine derivatives in various ratios and positive results were obtained (Tab.6).

Catalytic activity increases by taking a mixture of complexes in various ratios, which has a positive effect on the yield of the resulting acid mixture. Thus, maximum yield is 34% by using these complexes separately, but the yield a mixture is more than 40%.

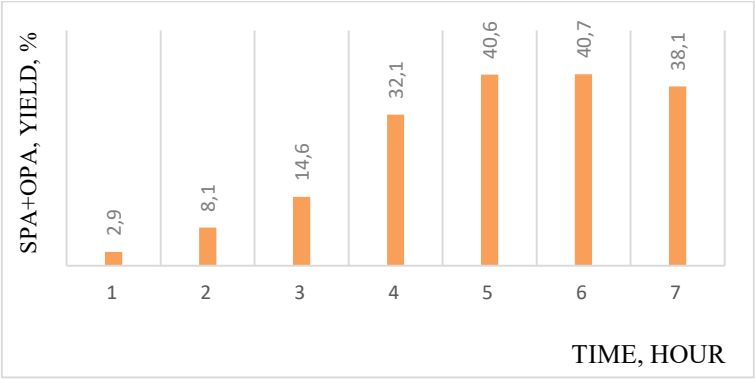


Fig.6. Time dependence of oxidation process in the presence of 2,4 –DNPH complexes of $Cr(acac)_3$ and $Co(acac)_2$ in 3:1 ratio

As is evident from Fig. 6, the SPA+OPA mixture obtained by 5-hour process possesses the optimal yield. Therefore, it should be noted that the reaction time is 5 h, and the catalyst concentration is 0,2% mas. (relative to the raw material) as an optimal condition for the oxidation of naphthene-paraffinic hydrocarbons in the presence of 2,4-DNPH complexes of $Cr(acac)_3$ and $Co(acac)_2$ in the ratio of 3:1.

For the purpose of increasing the yield of SPA and OPA, oxidation process of a non-soapy part (NSP), i.e. a non-neutralized part of the oxidate (non-oxidized hydrocarbons and other oxidation products) was carried out and high results were obtained in catalytic presence of the mixture of 2,4-DNPH complex of $Cr(acac)_3$ and 2,4-DNPH complex of $Co(acac)_2$ in a ratio of 3:1 ratio. This allowed doubling the yield of SPA. For this purpose, NSP, its mixture with dearomatized diesel fraction was taken in a ratio of 1:1 and 3:1 by mas. (Tab. 7). The process was carried out in 5 h with a catalyst content of 0,2% mas.

Table 7. Results of oxidation process of the non-soapy part in the catalytic presence of a mixture of 2,4-DNPH complexes of $Cr(acac)_3$ and $Co(acac)_2$ in a ratio of 3:1

Raw material	SPA		OPA		SPA+OPA
	Yield, %	Acid number, mgKOH/g	Yield, %	Acid number, mgKOH/g	Yield, %
Naph.-par. and NSP = 1:3	14,8	130	19,5	109,2	34,3
NSP	16,5	156,8	22	124	38,5
Naph.-par.and NSP = 1:1	14,2	111,9	19,5	119,4	33,7
Naph.-par.and NSP = 1:2	14,4	120,2	20,2	110,5	34,6

Tab. 7 shows that the results obtained by aerobic oxidation process in the presence of a catalytic system consisting of a mixture of 2,4-DNPH complex of $Cr(acac)_3$ and 2,4-DNPH complex of $Co(acac)_2$ in a ratio of 3:1 don't lag behind the results of the oxidation of naphthene-paraffinic hydrocarbons. If we take into account that the yield of the acid mixture obtained by the oxidation of naphthene-paraffinic hydrocarbons in the presented catalytic system is 40,6%, but 38,5% by the oxidation of NSP, we can prove obtaining SPA+OPA with a yield of 79,1% from both stages. This is a very high figure in comparison to previous investigations.

Spectroscopic study of time dependence of catalytic oxidation process of naphthene-paraffinic hydrocarbons

For the purpose of studying oxidation process of dearomatized diesel fraction, their IR spectra were recorded by taking samples at intervals of one hour during the process. Formation of oxidation products by increasing reaction time was observed by accumulation of carbonyl groups during the process. Absorption bands corresponding to the valence vibrations of C=O group were observed in the IR spectrum of the sample taken at one hour interval at 1715 cm^{-1}, 1777 cm^{-1} during the oxidation process. Comparing the IR spectra of the samples taken after one and three hours, it can be concluded that an increase in the intensity of the absorption band 1715, 1777 cm^{-1} was

observed in the last spectrum. Based on the IR spectra of the samples taken at the 3rd, 4th, 5th and 6th hours of the oxidation process, it can be noted that the intensities of the absorption bands of 1715, 1777 cm^{-1} increase by time dependence.

Valence vibrations of C-O and C=O groups occur in the absorption bands 1168 cm^{-1} and 1713 cm^{-1} in the 1st hour of the oxidation process carried out in the catalytic presence of 2,4-DNPH complex of $Mn(acac)_2$. In the 2nd hour of the process, along with the increase in the intensity of the absorption bands at 1169 and 1714 cm^{-1} (C=O group), valence vibrations corresponding to the C-O bond at 1242 cm^{-1} absorption bands are observed. Along with the increase in the intensity of the absorption bands shown in the 3rd hour of the oxidation reaction, deformation vibrations of O-H bond are observed in the absorption band 937 cm^{-1}. 4, 5 and 6 hours after beginning of the oxidation process, an increase in intensity can be easily seen in all absorption bands of the above-mentioned oxygen-containing bonds. In the 7th hour of the process, an increase isn't observed in the intensity of these absorption bands. It should be noted that all the absorptions that occur in the 1-7th hours of the process in the absorption bands of 3000-3600 cm^{-1} corresponds to O-H bond of acid.

The values of the optical densities of the absorption bands of H-O, C-O, C=O bonds depending on the reaction time are presented in Tab.8.

Table 8. Time dependence of optical densities of absorption bands of H-O, C-O, C=O bonds

Samples	D_{937}(OH)	D_{1169}(C–O)	D_{1714}(C=O)	D_{1242}(C–O)
NPH	–	–	–	–
The 1st hour	–	0,018	0,029	–
The 2nd hour	–	0,038	0,064	0,036
The 3rd hour	0,029	0,059	0,097	0,053
The 4th hour	0,036	0,082	0,130	0,071
The 5th hour	0,041	0,097	0,146	0,081
The 6th hour	0,049	0,117	0,170	0,095
The 7th hour	0,050	0,119	0,170	0,096

The table shows that it isn't sufficient to continue the oxidation process of NPH for 7 hours. The obtained results coincide with the experimental results.

Determination of particle sizes in different catalytic systems

Dynamic light scattering (DLS) was used to determine the distribution and size of the catalyst crystals (crystal sizes were measured using LB 550, Horiba analyzer). Determination of the size of the catalyst particles during NPH oxidation process in the presence of $Mn(acac)_2$ was explained in more detail: DLS spectra of the liquid phase system consisting of naphthene-paraffinic fraction and $Mn(acac)_n$ dispersed in the fraction were presented before the reaction and 1, 4, 5 hours after the reaction.

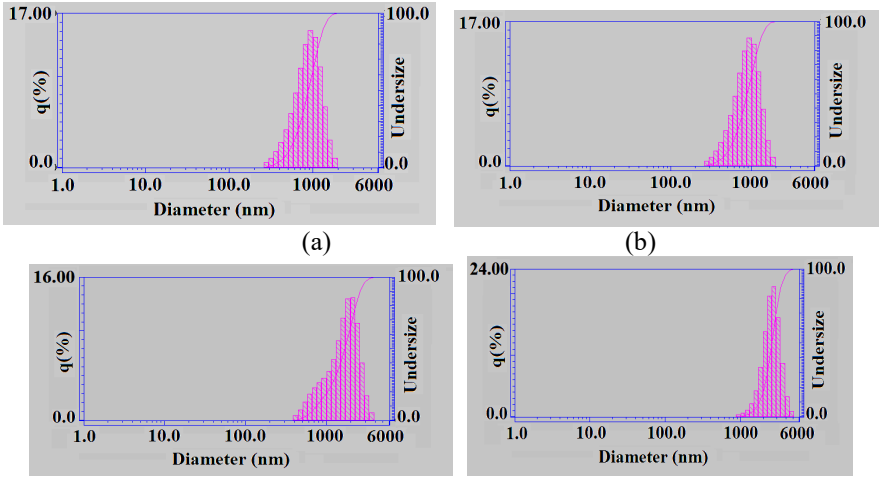


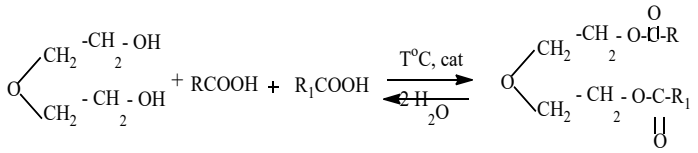
Fig. 7. DLS histograms of a system consisting of NPH and a dispersed Mn(II) acetylacetonate complex: a) before the reaction, (b, c, d) after the reaction, respectively, 1 hour, 4 hours and 5 hours

The catalytic composition can be described as a micro- and nanoscale disperse system with a "hydrodynamic diameter" of 0,7-2,6 μm. In the oxidation process with $Mn(acac)_2$, the average size of the catalyst particles was 0,7 μm in the 1st hour of the reaction, 0,9 μm in the 1st hour of the reaction, 1,7 μm in the 4th hour, and in the 5th hour increased to 2,6 microns. As mentioned above, this change can be

explained by the relationship between the catalyst and the reaction products.

Synthesis of mixed diesters of petroleum- and fatty acids-based diethyleneglycol in the presence of heterogeneous catalysts, study of their properties

The ethers were synthesized by the following reaction using SPA, valeric acid and diethylene glycol (DEG) as raw materials:



here: R- SPA; R_1 - C_4H_9 radicals.

As the asymmetric esters of DEG on the basis of petroleum and valeric acids correspond to the parameters of plasticizers according to their physical and chemical properties, mixing of these diesters in polyvinylchloride (PVC) was studied in laboratory conditions: the compositions were developed by adding 30-70 mas. fraction of test diesters to 100 mas. fraction of PVC, 1 mas. fraction of stabilizer (calcium stearate) and these compositions were kept in a thermostat at 65ºC, 75ºC, 85ºC for 3-6 hours depending on the temperature. After the compositions had cooled to room temperature and kept under a load of half a kilogram on filter paper for 12 h, the optimal mix of test ethers (40 mas.fraction) was determined and defined to be recommended as primary and auxiliary plasticizers for polymeric materials.

Simultaneously, for the purpose of reducing the amount of sediment characterizing the thermooxidation stability of DF, the synthesized mixed diesters have been tested in the ЛСАРТ laboratory apparatus at 120°C for 4 hours with the addition of 0,004% in 100 ml DF and a decrease was observed in the amount of sediment from 6,0 mg/100cm^3 to 0. Ethyleneglycol α-naphthyl ester of SPA synthesized in the presence of N-methylpyrrolidone hydrosulfate catalyst also reduced the amount of sediment from 2.4 mg to 0,00. These results confirm that the synthesized mixed diesters can be used as effective

antioxidants.

Study of bactericidal properties of amidoamines, imidazolines and their complexes of synthetic petroleum and oxyacid mixtures

Amidoamines with inhibitory-bactericidal properties were synthesized on the basis of synthesized SPA+OPA and polyethylene polyamines (PEPA). Effect of synthesized amidoamine and its complexes with organic and inorganic acids (amidoamine - T-1, amidoamine complex with HB - T-2, amidoamine complex with HNO_3 - T-3, amidoamine complex with HCOOH - T-4, amidoamine complex with CH_3COOH - T-5) on the vital activity of SRB was studied using "*Desulfovibrio desulfuricans*" species and strain 1143 of SRB.

Effect of reagents on the vital activity of SRBs at concentrations of 25, 50, 125 and 250 mg/l is presented in Fig. 8.

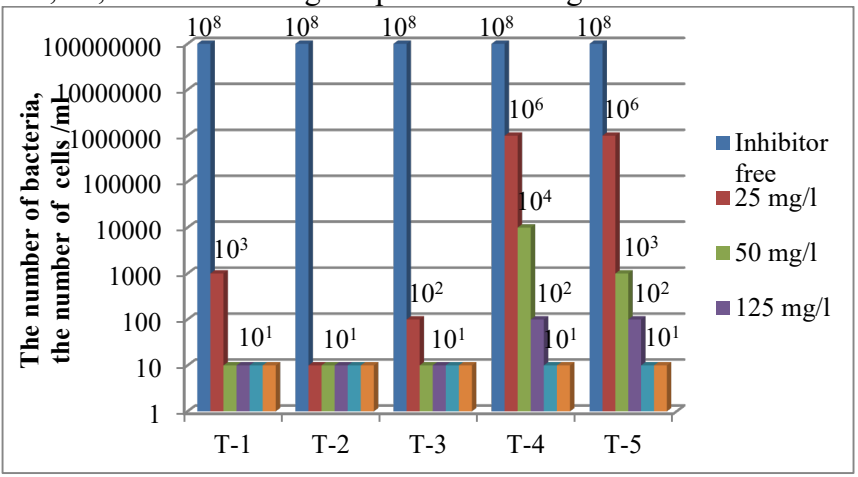


Fig.8. Effect of the samples T-1, T-2, T-3, T-4 and T-5 in various concentrations on the number of SRB

As is evident from the diagram, the number of bacteria in an inhibitor-free environment is $n=1\times 10^8$, this number is reduced from 10^8 to 10^1 (from one hundred million to 10) at a concentration of 50 mg/l in an environment with T-1, T-2, T-3 inhibitors, from 10^8 to 10^4 (from one hundred million to 10.000) for T-4 sample, and from 10^8 to

10^3 (from one hundred million to one thousand) for T-5 sample. At 250 and 500 mg/l, the number of bacteria is reduced from 10^8 to 10^1 for all samples. At the end of the study, the samples were titrated by iodometric method and the protective effect was calculated according to the amount of H_2S. T-1, T-2, T-3 samples have a bactericidal effect of 90-93% at a concentration of 125 mg/l and 94,5-96,4% at a concentration of 250 mg/l. T-4 and T-5 complexes have a biocidal effect (90-91%) at a concentration of 250 mg/l that partially affects the vital activity of SRB. All samples possess 93-98% bactericidal effect at a concentration of 500 mg/l.

Simultaneously, imidazolines based on SPA+OPA and PEPA were synthesized, their HCl and CH_3COOH complexes were developed and bactericidal effect was tested. Complexes of synthesized imidazoline with HCl, HBr, HNO_3 and CH_3COOH acids in a ratio of 1:1 were obtained at room temperature, 20% isopropyl alcohol was selected as a solvent for the complexes. (**Note:** N-1-imidazoline synthesized on the basis of SPA+OPA and PEPA, N-2 - HCl, N-3 - HBr, N-4 - HNO_3, N-5 - CH_3COOH complexes of imidazoline in a ratio of 1:1). A graphical description of the effect of the complexes on the growth of SRB at concentrations of 25, 150 and 250 mg/l is given in Fig. 9.

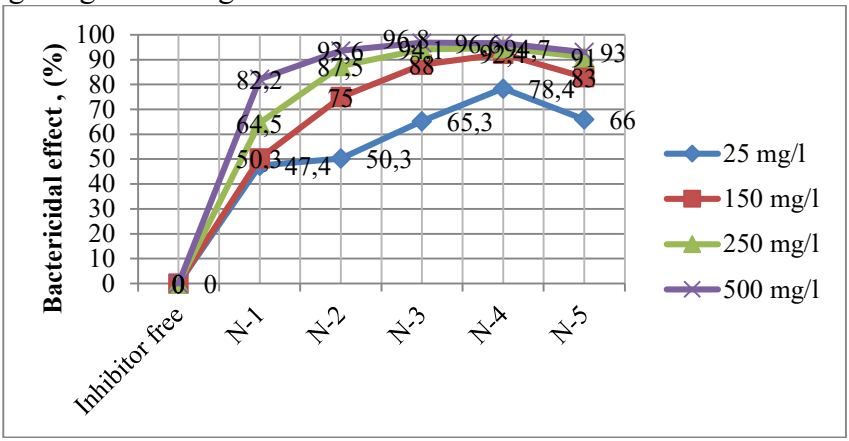


Fig. 9. Graphical description of bactericidal effect of the samples N-1, N-2, N-3, N-4, N-5 on the growth of SRB

N-1, N-2, N-3, N-4, N-5 complexes possess 47,4-78,4% bactericidal effect at a concentration of 25 mg/l, 50,3-92,4% at a concentration of 150 mg/l, 64,5-94,7% at a concentration of 250 mg/l, 82,2-96,8% at a concentration of 500 mg/l and prevented SRB growth. As a result of the studies, it was determined that in comparison to synthesized imidazolines, the complexes based on them have a higher bactericidal effect and prevent the development of sulfate-reducing bacteria.

Thus, it was determined that it's possible obtaining high-yield, selective and high-quality synthetic organic acids and high-quality reagents based on these acids by aerobic oxidation of petroleum hydrocarbons in the catalytic presence of acetylacetonates of transition metals and their 2,4-dinitrophenylhydrazine complexes.

CONCLUSIONS

1. For the first time, naphthene-paraffinic hydrocarbons separated from the fraction of mixed oils boiling at 185-329°C taken from the Heydar Aliyev Baku Oil Refinery were oxidized by atmospheric oxygen in liquid phase in the catalytic presence of acetylacetonates of transition metals (Cr, Co, Mn, Zn, Ni). In this case, the highest results were obtained by Mn- and Cr-acetylacetonates. Thus, the yield of obtained SPA+OPA was 33% and 22.1% at 0,3% wt. of the concentration of catalysts according to the raw material. Mixture of Cr- and Mn-acetylacetonates in various ratios taken as catalysts for the oxidation process causes an increase in the yield of SPA+OPA up to 35% due to the synergistic effect. In this case, the optimal conditions were as follows: reaction time - 5 hours, catalyst - $Cr(acacs)_3$:$Mn(acac)_2$ = 3:1 mas. mixture (0.2% mas. of raw material) [1, 5, 7, 10, 15].
2. For the first time it was determined that 2,4-dinitrophenylhydrazine complexes of metal-diketonates of transition metals and their mixture in various ratios possess an effective catalytic effect on obtaining high yield SPA+OPA. Thus, the yield of SPA+OPA was 34% by taking 2,4-

dinitrophenylhydrazine complex of $Mn(acac)_2$ in 0,2% mas. according to raw material. But the yield of SPA+OPA was 40,6% obtained by the oxidation process carried out for 5 hours in the presence of a mixture of 2,4-DNPH complexes of $Cr(acac)_3$ and $Co(acac)_2$ in a ratio of 3:1 [11, 14, 20].

3. For the purpose of increasing the yield of SPA and OPA, oxidation process of non-saponified part (NSP) was carried out in the catalytic presence of a mixture of the complexes of 2,4-DNPH with $Cr(acac)_3$ and $Co(acac)_2$ in a ratio of 3:1 and high results were obtained. NSP and its mixture with dearomatized diesel fraction were taken in the ratios 1:1, 2:1 and 3:1. The yield of the acid mixture obtained by the oxidation of naphthene-paraffinic hydrocarbons via the presented catalytic system was 40,6%, but it was 38,5% by the oxidation of the non-soapy part, the yield of the acid mixture obtained from both stages was 79,1%.
4. The optimal catalytic components for the oxidation process are a mixture of $Cr(acacs)_3$:$Mn(acac)_2$=3:1 mas. and a mixture of 2,4-DNPH complexes of $Cr(acac)_3$ and $Co(acac)_2$ in a ratio of 3:1 (0.2% mas. of raw material). Spectroscopic determination of time dependence of the catalytic oxidation process of naphthene-paraffinic hydrocarbons was studied. The results obtained were the same as the experimental results. The distribution and determination of particle sizes of in various catalytic compositions were studied using the dynamic light scattering (DLS) [24].
5. Mixed diesters based on diethylene glycol with SPA and valerenic acids, as well as triethylene glycol with SPA and caproic acids were synthesized and these esters were recommended as basic and auxiliary plasticizers for polymeric materials. The synthesized mixture was tested in the ЛСАРТ laboratory apparatus at 120°C for 4 hours with the addition of 0,004% concentration in 100 ml of DF and it was observed that the sediment amount decreased from 6,0 mg/100 cm^3 to 0 [3, 9, 18].
6. For the first time, ethylene glycol α-naphthyl ester of SPA was

synthesized in the presence of ionic liquid (N-methylpyrrolidone hydrosulfate) catalyst, physical and chemical parameters were determined. The sediment amount was reduced from 2,4 mg to 0,00 mg by adding the synthesized ether to 100 ml of hydropurified diesel fuel at a concentration of 0,004%. As a result, the possibility of using the synthesized ether as an effective antioxidant improving thermoxidation stability of DF was demonstrated [17, 19, 21].

7. Amidoamines, imidazolines were obtained on the basis of synthesized SPA+OPA and PEPA in a ratio of 1:1 mol, their complexes with organic and inorganic acids (HBr, HNO_3, CH_3COOH, HCOOH) were developed and their effect on "*Desulfovibrio desulfur*" species of SRB was studied in microbiological corrosion environment. It was determined that complexes of amidoamines with inorganic acids possess higher bactericidal effect (bactericidal effect at a concentration of 125 mg/ l, respectively, 93 and 92,8%; 97,8 and 98% at a concentration of 500 mg/l); imidazolines possessed bactericidal effect of 82,2%, complexes of imidazoline derivatives with inorganic acids ~93-97% at a concentration of 500 mg/l, and its complex with acetic acid 93% [22, 23].

The scientific papers published on the main content of the dissertation:

1. Abbasov, V.M. Aliyeva, L.I., Afandiyeva, L.M. Babanly, N.N., Aliyev, B.M., Yusifov, R.M., Tahirova, F.F. Catalytic Effect of Mn (III), Cr (III) Acetylacetonate Salts on Oxidation Process of Petroleum Hydrocarbons //International scientific conference "Actual Problems of Contemporary Natural and Economic Sciences" dedicated to National Leader Heydar Aliyev's 95 th anniversary of birth, Ganja: - May 04-05, -2018, -p. 222-224

2. Afandiyeva, L.M., Abbasov, V.M., Aliyeva, L.İ., Babanly N.N., Ahmadbayova, S.F., Rustamli, G.Y. Liquid Phase Oxidation of Naphthene-Paraffinic Hydrocarbons of Diesel Fraction in the Catalytic Presence of Reduced Graphene Oxide // 7th Rostocker International Conference: "Thermophysical Properties for Technical Thermodynamics" Thermam, Rostock, Germany:. -(July 26-27), -2018, -p. 59

3. Sadiyeva, N.F., Afandiyeva, L.M., Isgadarova, S.A., Babanly, N.N., Aghayev, B.K., Asadova, Sh.N., Musayeva, A.P., Aghdamski, T.A. Synthesis of mixed esters of diethyleneglycol in the presence of ZnO catalyst // International scientific-practical conference "Innovative Prospects for the Development of Oil Refining and Petrochemistry", dedicated to academician V.S.Aliyev's 110th anniversary of birth. Baku: - October 9-10, - 2018, - p. 34

4. Aliyeva, L.I., Abbasov, V.M., Afandiyeva, L.M., Babanly, N.N., Talybov A.H., Valiyeva, F.M., Musayeva, A.P., Aghdamski, T.A. Optimization of Aerobic Oxidation Process of Naphthene-Paraffinic Fraction of Petroleum // International scientific-practical conference "Innovative Prospects for the Development of Oil Refining and Petrochemistry", dedicated to academician V.S.Aliyev's 110th anniversary of birth. Baku: - October 9-10, - 2018, - p. 155

5. Aliyeva, L.I. Optimization of Deep Aerobic Oxidation of Naphthene-Paraffinic Fraction of Petroleum / L.I.Aliyeva, L.M.Afandiyeva, V.M.Abbasov, F.M.Veliyeva, N.N.Babanly, V.Kh.Musaly, F.N.Seyidahmadova // Oil Refining and Petrochemistry, - 2018. No 7, - p. 41-46

6. Afandiyeva, L.M. Study of Bactericidal-Inhibitory

Properties of Amidoamines, Imidazolines and Their Complexes Obtained on the Basis of Synthetic Oxy-, Petroleum-Acids / L.M.Afandiyeva, L.A. Mahmudova, A.R. Azizbayli, N.N. Babanly, V.Kh. Musaly // Proceedings of Azerbaijan High Technical Educational Schools. Azerbaijan, Baku: -2018. Vol. 20. No 2,33-37 p.

7. Aliyeva, L.I., Afandiyeva, L.M., Talybov, A.H., Babanly, N.N., Isayeva, Kh.A., Ahmadova, G.A. Study of Acetylacetonates of Transition Metals as Catalysts in Oxidation Process of Petroleum Hydrocarbons // Proceedings of scientific conference "Naghiyev Readings" dedicated to academician Murtuza Naghiyev's 110th anniversary of birth, Baku: -2018, -p. 146

8. Aliyeva, L.I. Optimization of Aerobic Oxidation of Naphthene-Paraffinic Hydrocarbons Separated From Diesel Fraction / L.I.Aliyeva, V.M.Abbasov, L.M.Afandiyeva F.M.Veliyeva, N.N.Babanly, L.A.Makhmudova, G.Y. Rustamly //Processes of Petrochemistry and Oil Pefining (PPOR), - 2018. V.19, №3 (65), - p. 245-254

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