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**ABSTRACT**

of the dissertation for the degree of Doctor of Philosophy

**STUDY OF OBTAINING PROCESS OF SYNTHETIC  
PETROLEUM ACIDS FROM 190-330°C PETROLEUM  
FRACTION IN THE PRESENCE OF ALUMINUM  
OXIDE-BASED CATALYSTS**

Speciality: 3321.01 – Petroleum-gas-hard coal processing and  
technology

Field of science: Chemistry

Applicant: **Gulay Yusif Rustamli**

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The work was performed at the laboratories "Liquid Phase Oxidation", "Corrosion Inhibitors and Conservative Materials" and "Catalytic Cracking and Pyrolysis" of academician Y.H. Mammadaliyev Institute of Petrochemical Processes of the Ministry of Science and Education of the Republic of Azerbaijan.

Scientific supervisors: Doctor of technical sciences, professor  
**Hikmat Jamal Ibrahimov**

Doctor of chemical sciences,  
associate professor

**Lala Mahammad Afandiyeva**

Official opponents:

Doctor of chemical sciences, professor

**Chingiz Knyaz Rasulov**

Doctor of chemical sciences, professor

**Gasim Zulfali Huseynov**

Doctor of philosophy in chemistry

**Aynura Anvar Aliyeva**

One-time Dissertation council BFD 1.16 on the base of Dissertation council ED 1.16 of Supreme Attestation Commission under the President of the Republic of Azerbaijan operating at academician Y.H. Mammadaliyev Institute of Petrochemical Processes of the Ministry of the Republic of Azerbaijan

Chairman of the Dissertation Council:

Doctor of chemical sciences,  
academician

**Vagif Maharram Abbasov**

Scientific Secretary of the Dissertation Council:

Doctor of chemical sciences,  
associate professor

**Lala Mahammad Afandiyeva**

Chair of the scientific seminar:

Doctor of chemical sciences,  
professor

**Safa Islam Abasov**

## GENERAL CHARACTERISTICS OF THE WORK

**Relevance and elaboration level of the topic.** Currently, carbonic acids are of great importance as raw materials for industrial production of various products in many areas of the national economy. Petroleum carbonic acids occupy a special place among these acids, widely used in paint industry and in production of detergents, plasticizers, flotation agents, fuel additives, etc. Natural organic acids are mainly found in free form in petroleum. Vegetable oils mainly contain triglycerides of saturated and unsaturated fatty acids. Obtaining these acids by hydrolysis occurs by several steps, on the other hand, because of the increasing food problem, the use of vegetable oils for technical purposes is not considered acceptable. On the other hand, the freezing points of products synthesized on the basis of acids obtained from vegetable oils are quite high, and the product itself is not stable during storage due to double bonds in acid radical.

Although natural petroleum acids have stability and a very low freezing point, they are not present in any petroleum or their amount is limited. It should be noted that one of the simple, widespread processing methods of hydrocarbons is their oxidation with molecular oxygen, which is quite appropriate for obtaining organic acids with a wide range of applications. Since the 60s of the last century, conversion of petroleum hydrocarbons into synthetic organic acids with the same field of application of natural petroleum acids has been widely studied by researchers via catalytic oxidation in liquid phase. According to the above, synthesis of synthetic petroleum acids on the basis of the petroleum fraction dominated by naphthenic hydrocarbons is of both scientific and practical importance<sup>12</sup>. However, despite large-scale studies carried out in this field, synthesis of synthetic petroleum acids with high yield still remains an actual problem. For this reason, systematic and

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<sup>1</sup> 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.

<sup>2</sup> Abbasov, V.M. Chemistry of cycloalkanes / V.M.Abbasov, R.A. Jafarova, L.M. Afandiyeva [et al.]. Baku: Muallim, -2019. - 385 p.

comprehensive study of synthetic petroleum acids is of great importance along with natural petroleum acids.

So, development of new, effective catalytic systems for the synthesis of synthetic petroleum acids on the basis of petroleum fraction dominated by naphthenic hydrocarbons boiling at 190-330°C, improvement of the efficiency of oxidation processes, selection of optimal conditions for the process, study of the composition of synthesized acids and the work on the basis of these acids carried out in the direction of the synthesis and study of efficient multifunctional reagents is important for the solution of certain theoretical issues and the creation of more efficient industrial products.

**The object and subject of the research.** The object of the dissertation is the synthesis of synthetic petroleum and oxyacids (SPA and OSPA) by catalytic oxidation of naphthene-paraffinic hydrocarbons separated from the mixture of Azerbaijani petroleum in liquid phase in the presence of air oxygen, but the subject is the determination of practical and versatile ways of using the synthesized synthetic organic acids mixture.

**The goals and objectives.** The main goal of the study is synthesis and application of new, reusable catalytic systems for the synthesis of synthetic petroleum and oxyacids as a result of dearomatization and liquid-phase oxidation of the petroleum fraction boiling at 190-330°C, as well as the synthesis of substances with various effective applications on the basis of a mixture of synthesized organic acids.

- Dearomatization of petroleum fraction boiling at 190-330°C by sulfonation method and determination of structural groups of obtained naphthene-paraffinic hydrocarbons using IR and  $^1\text{H}$  NMR spectra;
- study of liquid-phase aerobic oxidation process of naphthene-paraffinic hydrocarbons with catalytic participation of individual and mechanical mixtures of monometallic catalytic systems of nano  $\gamma\text{-Al}_2\text{O}_3$  modified with salts of variable valence metals (Mn, Co, Cr);
- study of liquid-phase aerobic oxidation process of naphthene-paraffinic hydrocarbons with catalytic participation of the

individual and certain ratio mechanical mixture of nano  $\gamma$ - $\text{Al}_2\text{O}_3$  bimetallic catalytic systems modified with salts of Mn, Co, Cr;

- study of reuse of mono- and bimetallic modifications of nano  $\gamma$ - $\text{Al}_2\text{O}_3$  used as a heterogeneous catalyst during liquid-phase aerobic oxidation of naphthene-paraffinic hydrocarbons in oxidation process;
- determination of the optimal parameters of catalytic oxidation process of naphthene-paraffinic hydrocarbons and formal kinetic regularities of time dependence;
- determination of particle sizes of catalysts used in liquid-phase oxidation process;
- synthesis of nitrogenous derivatives of synthesized synthetic organic acids mixture and study of inhibitory and bactericidal properties of those compounds against  $\text{CO}_2$  corrosion.

**Research methods.** As a result of the oxidation process, synthetic petroleum acid mixture was synthesized in the bubbler unit during the research conducted in accordance with modern methods and standards. Physicochemical properties and structure of the diesel fraction used as raw material during the process before and after dearomatization, as well as the synthesized acids and their nitrogenous derivatives were confirmed by modern spectroscopic methods – IR and  $^1\text{H}$  NMR. Thermal analysis, X-ray phase analysis and SEM were used for the purpose of studying the structure of catalysts. Dynamic light scattering method was used to measure the particles.

**The main provisions submitted for defense.** Aerobic oxidation process of naphthene-paraffinic hydrocarbons was studied with catalytic presence of  $\gamma$ - $\text{Al}_2\text{O}_3$  modified with salts of Mn, Cr, Co metals. Mixture of synthetic organic acids was obtained with a high yield, aminoesters, Ba, Al salts, and imidazolines were synthesized on the basis of the acids and their complexes with organic acids were developed. Synthesized aminoesters, salts and complexes were studied as corrosion-bactericidal inhibitors and recommended as efficient reagents with high effect.

### **Scientific novelty of the research.**

- For the first time, liquid-phase oxidation of naphthene-paraffinic hydrocarbons with air oxygen was carried out in the catalytic presence of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> modified with salts of transition metals (Mn, Co, Cr) and synthetic organic acids were obtained with a high yield;
- it was determined that synergistic effect occurs during the oxidation process with a mixture of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (monometallic) catalysts modified with metal salts of Mn, Cr, Co in different proportions, and the yield of the mixture of synthetic organic acids obtained at this time amounts to 44.4% maximally;
- among the catalytic systems, the maximum yield of synthetic organic acids was achieved by the use of bimetallic composite nanoparticles of nano  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> modified with salts of variable valence metals such as Mn, Co, Cr (45.2%);
- aminoesters on the basis of synthetic petroleum acids and ethanolamines (MEA, DEA and TEA), as well as complexes of imidazoline derivatives of a mixture of synthetic organic acids (SPA and OSPA) with organic acids were developed and the long-term effect of each of them was studied as an inhibitor against CO<sub>2</sub> corrosion;
- bactericidal-inhibitory properties of aminoesters of SPA on the basis of MEA, DEA and TEA and metal (Ba and Al) salts of SPA were studied and their high bactericidal effect was determined.

### **Theoretical and practical significance of research.**

Aminoesters obtained on the basis of synthetic petroleum acid may be recommended for application as effective corrosion inhibitors. Thus, the use of aminoesters synthesized on the basis of synthetic petroleum acid and ethanolamines at a concentration of 100 mg/l creates a protective effect of 99.2-99.5% against corrosion in metal structures within 20 hours. Simultaneously, both aminoesters and complexes of imidazoline derivatives of a mixture of synthetic acids have a long-term effect against corrosion. So, at the end of the 433rd hour, the followings were observed against CO<sub>2</sub> corrosion: protective effect of SPA and MEA-based aminoester was 95%, SPA and DEA-

based aminoester - 94.6%; CH<sub>3</sub>COOH complex of imidazoline derivatives of SPA and OSPA mixture had 95.5% and HCOOH complex - 97% protective effect. These compounds are confirmed to be used as effective corrosion inhibitors.

Effect of aminoesters and Ba, Al salts synthesized on the basis of SPA on biocorrosion process was determined. Possibility of applying the compounds as an effective bactericidal inhibitor was proved. Thus, bactericidal effect of SPA- and MEA-based aminoester synthesized at 600 mg/l is 99.1%; SPA- and DEA-based aminoester show 100% bactericidal effect, SPA- and TEA-based aminoester - 95.2%; Ba salt of SPA showed 100% and Al salt - 100% bactericidal effect at a concentration of 500 mg/l.

**Personal involvement of the author.** The author directly participated in the implementation of laboratory experiments, the systematic collection of literature related to the topic, the systematization of conducted research, writing and compilation of theses and articles related to the dissertation.

**Approbation and application.** 17 scientific works, including 8 articles and 9 theses, were published on the dissertation work.

The main results related to the dissertation were presented and discussed at the following scientific conferences: "Students' 1st Republican Scientific Conferences" dedicated to the the national leader Haydar Aliyev's 96th anniversary (Baku, 2019), the International Scientific Conference "Actual Problems of Contemporary Natural and Economic Sciences" (Ganja, 2019), International Chemistry Conference (Turkey, Istanbul, 2019), International Scientific Conference "Current Problems of Modern Chemistry" dedicated to the 90th anniversary of the Academician Y.H. Mammadaliyev Institute of Petrochemical Processes (Baku, 2019), International Conference "Technical Thermodynamics: Thermophysical Properties and Energy Systems" (Germany, Rostock, 2020 - 2 theses), International Conference "Actual Problems in Chemical Engineering" dedicated to the 100th anniversary of ASOIU (Baku, 2020), Republican scientific conference "Modern Problems of Chemistry" dedicated to Nizami Ganjavi's 880th anniversary of the birth (Sumgayit, 2020),

Republican scientific conference "Catalysts, Olefin-based Oils" dedicated to academician Nadir Mir-Ibrahim oglu Seyidov's 90th anniversary of birth (Baku, 2022).

**The dissertation work was performed** at the laboratories "Liquid-Phase Oxidation", "Corrosion Inhibitors and Conservative Materials" and "Catalytic Cracking and Pyrolysis" of academician Y.H. Mammadaliyev Institute of Petrochemical Processes of the Ministry of Science and Education of the Republic of Azerbaijan.

**The structure and scope of the dissertation.** The dissertation consists of 205 pages, including introduction (11990 signs), 5 chapters (Chapter I - 63636 signs, Chapter II - 35551 signs, Chapter III - 58323 signs, Chapter IV - 25392 signs, Chapter V - 34694 signs), conclusions (3640 signs), 247 references including description of abbreviations and the total volume consists of 233229 signs (excluding figures, tables, graphs, appendices and bibliography). The dissertation includes 54 tables, 58 pictures and 1 scheme.

**Introduction** deals with the brief information on the relevance of the topic, scientific novelty of the research, the goals and tasks, practical importance, approbation of the work, research methods, structure and scope.

**The first chapter** analyzes the literature review given in the research works on the production and application areas of organic acids, liquid-phase oxidation of petroleum hydrocarbons, the catalysts used in the process, catalyst carriers and the properties.

**The second chapter** presents the preparation of raw materials for the purpose of obtaining a mixture of synthetic acids, the method for synthesis of the catalyst, physicochemical properties of the initial materials used in the oxidation reaction, study of their structural group composition and morphology by modern methods.

**The third chapter** is devoted to liquid-phase oxidation of naphthene-paraffinic hydrocarbons obtained by dearomatization of 190-330°C fraction of petroleum in the catalytic presence of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> modified with salts of transition metals with air oxygen. Both monometallic and bimetallic modifications of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, taken as a carrier, were used as catalysts in the oxidation process in the form of



individual and certain ratio mechanical mixtures. In addition, the mechanism of the oxidation process, physicochemical properties of the target products obtained from the process - synthetic organic acids, structural group composition, and factors affecting the oxidation process were studied in the chapter.

**The fourth chapter** determines the optimal parameters of the oxidation process, regression graphs, formal kinetic regularities of the time dependence of the oxidation process, and the sizes of the catalyst particles before and after the oxidation process.

**The fifth chapter** deals with the synthesis and properties of synthetic organic acids and aminoesters from their mixture, imidazoline derivatives and their complexes with organic acids, and metal salts of synthetic petroleum acid. SPA- and OSPA-based compounds were studied as inhibitors against CO<sub>2</sub> corrosion and biocorrosion.

The results, literature list, appendices, and abbreviations are listed at the end of the dissertation.

## **MAIN CONTENT OF THE WORK**

The fraction of the mixture of Azerbaijani petroleum boiling in the temperature range of 190-330°C was used in the studies as raw material for the synthesis of SPA brought from Haydar Aliyev Baku Oil Refinery. Physicochemical properties and structural group composition were determined before using the diesel fraction as raw material and after the dearomatization process carried out by the sulfonation method. It was determined that amount of aromatic hydrocarbons in the fraction decreases from ~20% to ~1.5% after sulfonation.

## **Study of liquid-phase oxidation process of naphthene-paraffinic hydrocarbons separated from the mixture of Azerbaijani petroleum in the presence of $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst modified with Mn, Cr, Co salts**

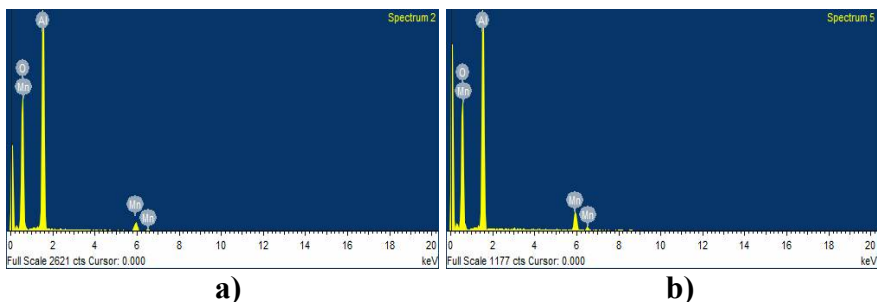
Liquid-phase aerobic oxidation of naphthene-paraffinic hydrocarbons separated from the diesel fraction boiling at 190-330°C was carried out in a bubbler-type device, in the temperature range of 135-140°C, in the presence of air oxygen supplied at a rate of 300 l/kg·h, for 5-6 hours. For the purpose of synthesizing  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> - as a carrier in the catalysts used in the process, the hydrolysis process of aluminum nitrate using the sol-gel method (using monoethanolamine (MEA) or diethanolamine (DEA) as a stabilizing agent during synthesis) was carried out by a known methodology<sup>3 4</sup>. In order to obtain  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, gel samples were thermotreated at different temperatures. The highest values of the pore volume were observed in samples annealed at 850°C. As a result of the study, it was determined that  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> has the highest specific surface when DEA is used as a hydrolyzing agent. This indicator is relatively low by using MEA. An increase in the mol ratio of OH<sup>-</sup> : Me<sup>+</sup> from 1 to 2 causes an increase in SSA value of volume of the samples micropores from 224 m<sup>2</sup>/g to 246 m<sup>2</sup>/g. These values vary as 211 m<sup>2</sup>/g and 218 m<sup>2</sup>/g, respectively, using MEA.

X-ray phase studies of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> synthesized by sol-gel method were carried out in X-Ray-TD 3500 (China) X-ray diffractometer, using a CuK $\alpha$  ( $\alpha=1.54184\text{\AA}$ ) radiation source and a Ni-filter 5-90° angle range, taken at room temperature.

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3 Danks, A.E., Hall, S.R., Schnepf, Z. The evolution of 'sol-gel' chemistry as a technique for materials synthesis // *Materials Horizons*, -2016. №3, -p.91-112.

4 Shaheen, I. Modified sol-gel synthesis of Co<sub>3</sub>O<sub>4</sub> nanoparticles using organic template for electrochemical energy storage / I. Shaheen, K.S. Ahmad, C. Zequine [et al.] // *Energy*, -2021. Vol.218, №119502, -p.1-9.



**Figure 1. X-ray fluorescence spectrum of a)  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (DEA) modified with 10% Mn compound and b)  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (DEA) modified with 20% Mn compound**

Figure 1 shows the morphology of the surface of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts modified with a) 10 and b) 20% Mn salt, X-ray element content expressed as a percentage on spectrum: a) the catalyst content is O - 49.37% mas., Al - 41.1% and Mn - 9.54%; b) the composition of the catalyst consists of O - 42.19%; Al - 38.35%, and Mn - 19.46% mas., and as is evident from the spectra, mass percentage of Mn increases in the composition of the catalyst by the increase in the amount of (CH<sub>3</sub>COO)<sub>2</sub>Mn•4H<sub>2</sub>O salt used in the modification of  $\gamma$ - Al<sub>2</sub>O<sub>3</sub>.

The catalyst amount calculated from the raw material was dissolved in a mixture of naphthene-paraffinic hydrocarbons of known weight, introduced into the bubbling unit, and followed by supplying the unit with air and a heating system, and the oxidation process was carried out.

Catalytic participation of the modifications of 10 and 20% mas. nano  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with the salts of Mn, Co, Cr transition metals was studied in liquid-phase oxidation of naphthene-paraffinic hydrocarbons with air oxygen in the presence of MEA as a stabilizer (Table 1).

Each of the catalysts used in the process was taken in an amount of 0.2% of the raw material, and each experiment was carried out in 5 hours at 135-140°C.

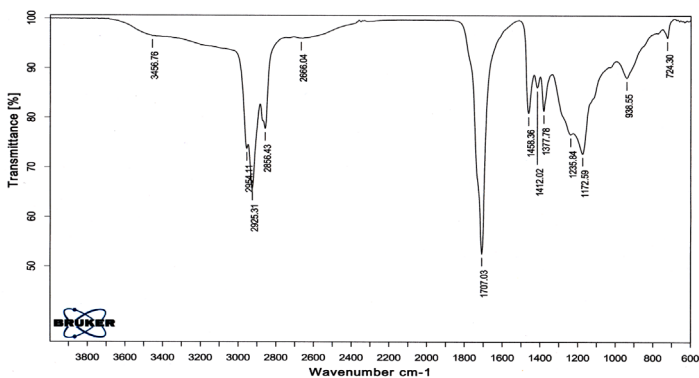
As is seen from Table 1, during the oxidation process carried out with the catalytic presence of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (MEA) modified with Mn, Cr, Co salts in the amount of 10% and 20% mas., the best result was

obtained in the catalytic presence of modification with Mn salt ( 30.5 and 34.1%).

**Table 1. Results of liquid-phase oxidation in the catalytic presence of  $\gamma\text{-Al}_2\text{O}_3$  (MEA) modified with Mn-, Co-, Cr-salts in the amount of 10% and 20% mas. of naphthene-paraffinic hydrocarbons**

Catalyst, 0.2% mas.	Oxidate		Yields of the products separated from oxidate, % (according to raw material)			
	Acid number, mgKOH/g	Yield, %	SPA	OSPA	SPA+OSPA	Non-saponifiable matter
10% Mn- $\gamma\text{-Al}_2\text{O}_3$	53.4	97.5	17.5	13.0	30.5	69.5
10% Co- $\gamma\text{-Al}_2\text{O}_3$	60.9	97.0	14.0	15.0	29.0	71.0
10% Cr- $\gamma\text{-Al}_2\text{O}_3$	66.5	98.2	12.5	9.5	22.0	78.0
20% Mn- $\gamma\text{-Al}_2\text{O}_3$	50.0	98.1	18.6	15.5	34.1	65.9
20% Co- $\gamma\text{-Al}_2\text{O}_3$	56.7	96.0	18.5	15.2	33.7	66.3
20% Cr- $\gamma\text{-Al}_2\text{O}_3$	53.1	98.2	17.2	15.0	32.2	67.8

The IR spectrum of SPA obtained as a result of the oxidation process is shown in Figure 2.



**Figure 2. IR spectrum of SPA obtained in the catalytic presence of nano  $\gamma\text{-Al}_2\text{O}_3$ (MEA) modified with 10% Mn**

The IR spectrum in Figure 2 allows to observe: the deformation and valence vibrations of the C-H bond of the CH<sub>3</sub> group at 724, 1377, 1412, 1458 cm<sup>-1</sup> and 2856, 2925, 2954 cm<sup>-1</sup>; 2666 cm<sup>-1</sup> valence vibrations of the COOH group belonging to the acid; 1707 cm<sup>-1</sup> valence vibrations of C=O bond of the acid group; valence vibrations of C-O bond belonging to the acid at 1172 cm<sup>-1</sup>; 938 cm<sup>-1</sup> and 3456 cm<sup>-1</sup> deformation and valence vibrations of O-H bond of the acid group, respectively. Thus, the IR spectrum confirms the presence of functional groups corresponding to SPA in the sample.

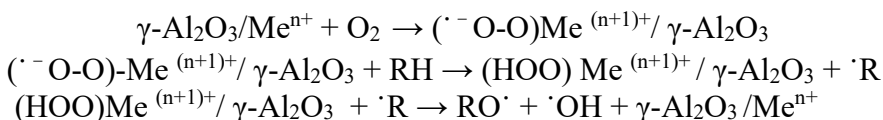
**Table 2. Physicochemical properties of SPA obtained from the oxidation process in the presence of nano  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>(MEA) modified with 20% Mn salt**

Properties	SPA
Density, at 20°C $\rho_4^{20}$ , kg/m <sup>3</sup>	960.5
Refractive index, $n_D^{20}$	1.4699
Kinematic viscosity, mm <sup>2</sup> /sec (at 50°C)	33.36
Kinematic viscosity, mm <sup>2</sup> /sec (at 80°C)	14.2
Sulfonation, % vol.	-
Iodine number, gI <sub>2</sub> /100 g	0.79
Acid number, mgKOH/g	185
Average molecular weight	303.24
Freezing point, °C	-46.3

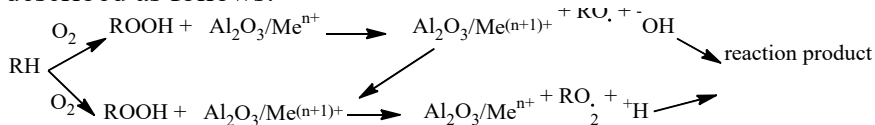
Physicochemical properties of SPA obtained from the oxidation process of naphthene-paraffinic hydrocarbons in the catalytic presence of nano  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (MEA) modified with 20% Mn are set into Table 2.

Also, physicochemical properties of obtained OSPA were determined: acid number=112.93 mgKOH/g,  $\rho$ =1022.5 kg/m<sup>3</sup>,  $T_{\text{freez.}}=-21^\circ\text{C}$ .

The mechanism of the oxidation reaction in the presence of nano  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> modified with metal salts is conventionally explained as follows:



The electron exchange caused by the catalytic participation of nano  $\gamma$ - $\text{Al}_2\text{O}_3$  modified with metal salts in the oxidation process is described as follows:



In the next experiments, effect of catalysts on the yield of desired products obtained from oxidation process was studied not individually but in a mechanical mixture (Table 3).

As is evident from Table 3, the highest yield of SPA+OSPA (SPA+OSPA=34.2%) using a mechanical mixture of catalysts in the ratio of 1:1, 1:2, 1:3 was obtained by the use of a mechanical mixture of catalysts in a ratio of 1:3. 1:3 ratio mixture of other catalysts was also used in oxidation process, since a higher result was obtained by a 1:3 mixture of catalysts.

**Table 3. Results of liquid-phase oxidation process in the catalytic presence of a mixture of  $\gamma$ - $\text{Al}_2\text{O}_3$  (MEA) catalysts modified with Co- and Cr- salts in a 20% mas. amount of naphthene-paraffinic hydrocarbons in different ratios**

No.	Catalyst mixture	Acid number of oxidate, mgKOH/g	SPA		OSPA		SPA + OSPA
			Yield, %	Acid number, mgKOH/g	Yield, %	Acid number, mgKOH/g	
1	20% Co- $\gamma$ - $\text{Al}_2\text{O}_3$ : 20% Cr- $\gamma$ - $\text{Al}_2\text{O}_3$ =1:1	49.0	12.6	118.0	11.0	110.0	23.6
2	20% Co- $\gamma$ - $\text{Al}_2\text{O}_3$ : 20% Cr- $\gamma$ - $\text{Al}_2\text{O}_3$ =1:2	50.0	16.4	119.0	13.1	114.4	29.5
3	20% Co- $\gamma$ - $\text{Al}_2\text{O}_3$ : 20% Cr- $\gamma$ - $\text{Al}_2\text{O}_3$ = 1:3	52.0	19.9	128.0	14.3	116.84	34.2

**Table 4. Catalytic participation of mono- and bimetallic modified nano  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>(MEA) with 10% and 20% Me in liquid-phase oxidation of naphthene-paraffinic hydrocarbons**

No.	Catalyst, 0.2% mas.	Oxidate		Obtained products					
		Acid number, mgKOH/g	Yield, %	SPA		OSPA		SPA+OSPA, %	Non-saponifiable matter
				Acid number, mgKOH/g	Yield, %	Acid number, mgKOH/g	Yield, %		
1	10% Mn- $\gamma$ -Al <sub>2</sub> O <sub>3</sub> : 10% Cr- $\gamma$ -Al <sub>2</sub> O <sub>3</sub> = 1:3	59.0	97.6	130.0	18.5	125.1	16.0	34.5	65.5
2	10% Co- $\gamma$ -Al <sub>2</sub> O <sub>3</sub> : 10% Cr- $\gamma$ -Al <sub>2</sub> O <sub>3</sub> = 1:3	52.44	99.88	122.93	19.1	120.36	11.0	30.1	69.9
3	20% Mn- $\gamma$ -Al <sub>2</sub> O <sub>3</sub> : 20% Cr- $\gamma$ -Al <sub>2</sub> O <sub>3</sub> = 1:3	60.1	97.4	120.5	20.9	119.1	18.0	38.9	61.1
4	20% Co- $\gamma$ -Al <sub>2</sub> O <sub>3</sub> : 20% Cr- $\gamma$ -Al <sub>2</sub> O <sub>3</sub> = 1:3	52.0	99.23	128.0	19.9	116.84	14.3	34.2	65.8
5	10% (Mn:Cr = 1:3) $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	55.0	98.7	113.3	19.6	121.3	16.4	36.0	64.0
6	10% (Co:Cr = 1:3) $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	53.0	97.5	138.0	17.5	146.0	15.0	32.5	67.5
7	20% (Mn:Cr = 1:3) $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	57.5	97.8	153.4	22.0	123.2	17.2	39.2	60.8
8	20% (Co:Cr = 1:3) $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	54.0	97.0	134.0	18.5	111.0	16.5	35.0	65.0

Note: The reaction was carried out in 5 hours at 135-140°C with an air supply rate of 300 l/kg·h.

1:3 mechanical mixture of various catalysts (No. 1, 2, 3 and 4) and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> modified with a 1:3 mixture of metal salts (bimetallic catalysts) (No. 5, 6, 7 and 8) were taken in the experiments presented in Table 4.

As is evident from Table 4, the yield of SPA+OSPA varies from 30.1 to 38.9% by the use of 1:3 mechanical mixtures of catalysts in the oxidation of naphthene-paraffinic hydrocarbons. It proves the creation of a synergistic effect during the joint use of catalysts and thus the increase of catalytic activity. Simultaneously, the use of a 1:3 mixture of salts on the carrier during modification slightly increased the yield of SPA+OSPA (32.5-39.2%).

**Study of liquid-phase oxidation process in the presence of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-based catalytic systems with diethanolamine as a stabilizer of naphthene-paraffinic hydrocarbons separated from the mixture of Azerbaijani petroleum**

The results of liquid-phase oxidation process of naphthene-paraffinic hydrocarbons in the presence of nano  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>(DEA) modified with 10 and 20% Mn-, Co-, Cr- salts are set into Table 5. The highest yield of SPA+OSPA – 40.6% is obtained in the presence of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>(DEA) catalyst modified with 20% Mn.

**Table 5. Results of liquid-phase oxidation process in the catalytic presence of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>(DEA) modified with 10% Mn-, Cr-, Co- salts of naphthene-paraffinic hydrocarbons**

Catalyst, 0.2 % mas. (considering the raw material)	Oxidate		Obtained products					
	Acid number, mgKOH/g	Yield, %	SPA		OSPA		SPA+OSPA, %	Non-saponifiable matter
			Acid number, mgKOH/g	Yield, %	Acid number, mgKOH/g	Yield, %		
$\gamma$ -Al <sub>2</sub> O <sub>3</sub> (DEA) mod. with 10% Mn	56.9	98.1	125.4	22.1	122.1	16.6	38.7	61.3
$\gamma$ -Al <sub>2</sub> O <sub>3</sub> (DEA) mod. with 10% Cr	41.3	95.2	119.8	19.8	106.2	14.9	34.7	65.3
$\gamma$ -Al <sub>2</sub> O <sub>3</sub> (DEA) mod. with 10% Co	51.1	95.4	126.3	16.0	122.9	13.7	29.7	70.3
$\gamma$ -Al <sub>2</sub> O <sub>3</sub> (DEA) mod. with 20% Mn	62.0	98.0	125.8	25.2	100.9	15.4	40.6	59.4
$\gamma$ -Al <sub>2</sub> O <sub>3</sub> (DEA) mod. with 20% Cr	48.0	98.4	132.8	22.5	120.57	16.7	39.12	60.8
$\gamma$ -Al <sub>2</sub> O <sub>3</sub> (DEA) mod. with 20% Co	53.6	97.0	128.2	23.0	118.0	15.0	38.0	62.0

Simultaneously, catalytic effect of the catalysts mixture in different proportions on the yield of SPA and OSPA in oxidation process of naphthene-paraffinic hydrocarbons was also studied and the results are presented in Table 6. As is evident, the use of 20%



Mn-modified  $\gamma\text{-Al}_2\text{O}_3$  (DEA) and 20% Cr-modified  $\gamma\text{-Al}_2\text{O}_3$  (DEA) catalysts in different proportions - 1:1, 1:2, 1:3 as mechanical mixtures produces SPA and OSPA with different yields from aerobic oxidation of paraffin hydrocarbons. In this case, the results of the combined use of catalysts are much higher.

Thus, when the catalysts are used separately, the average value of the yield of the mixture of acids obtained is 36.82%, this value is ~40% in joint use of the catalysts.

**Table 6. Results of liquid-phase oxidation process in the catalytic presence of a mixture of  $\gamma\text{-Al}_2\text{O}_3$  (DEA) modified with Mn- and Cr- salts in a 20% mas. amount of naphthene-paraffinic hydrocarbons in different proportions**

No.	Catalyst	Acid number of oxidatam mgKOH/g	SPA		OSPA		SPA+OSPA
			Yield, %	Acid number, mgKOH/g	Yield, %	Acid number, mgKOH/g	Yield, %
1	10% Mn- $\gamma\text{-Al}_2\text{O}_3$ :10% Cr- $\gamma\text{-Al}_2\text{O}_3$ = 1:3	52.2	23.0	132.0	17.9	117.0	40.9
2	10% Co- $\gamma\text{-Al}_2\text{O}_3$ : 10% Cr- $\gamma\text{-Al}_2\text{O}_3$ = 1:3	56.1	20.3	128.4	15.7	120.4	36.0
3	20% Mn- $\gamma\text{-Al}_2\text{O}_3$ : 20% Cr- $\gamma\text{-Al}_2\text{O}_3$ = 1:3	56.0	25.2	140.0	19.2	131.3	44.4
4	20% Co- $\gamma\text{-Al}_2\text{O}_3$ : 20% Cr- $\gamma\text{-Al}_2\text{O}_3$ = 1:3	50.0	21.2	125.5	18.8	112.2	40.0

In the next experiments, catalytic effect of bimetallic modifications of the synthesized  $\gamma\text{-Al}_2\text{O}_3$  (DEA) in the oxidation process was studied and the results are listed in Table 7. As is evident from Table 7, the highest yield of SPA+OSPA mixture – 46.8% was obtained in liquid-phase oxidation process of naphthene-paraffinic hydrocarbons in catalytic presence of (bimetallic) modified

nano  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (with DEA stabilizer) with a mixture of Mn and Cr-salts in the ratio of 1:3 in the amount of 20% mas.

**Table 7. Results of liquid-phase oxidation process of naphthene-paraffinic hydrocarbons in the catalytic presence of 10% and 20% bimetallic modified nano  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (DEA)**

Catalyst, 0.2 % mas. (considering the raw material)	Oxidate		Obtained products					
	Acid number, mgKOH/g	Yield, %	SPA		OSPA		SPA+OSPA, %	Nhon-saponifiable matter
			Acid number, mgKOH/g	Yield, %	Acid number, mgKOH/g	Yield, %		
10% (Mn:Cr = 1:3) $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	57.0	97.4	140.0	25.0	125.0	17.0	42.0	58.0
10% (Co:Cr = 1:3) $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	54.1	97.3	130.2	21.8	122.3	16.0	37.8	62.2
20% (Mn:Cr = 1:3) $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	60.5	98.6	142.3	26.8	128.5	20.0	46.8	53.2
20% (Co:Cr = 1:3) $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	56.0	98.0	135.4	23.2	123.6	19.3	42.5	57.5

### **Study of reuse of nano $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalytic systems modified with metal salts in the oxidation process of naphthene-paraffinic hydrocarbons**

It should be noted, that the catalysts used for the oxidation process were heterogeneous ones, so that they are insoluble in the substrate and can be easily separated and reused at the end of the reaction. The processes such as the synthesis and processing of these catalysts are carried out at high temperatures.

As a result of the oxidation process of naphthene-paraffinic hydrocarbons, synthesis of SPA and OSPA is carried out at 135-140°C, that is, at a temperature many times lower than the synthesis process of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> modifications with transition metals, so that the composition of the catalysts synthesized during the oxidation process

does not change depending on the temperature. Thus, the catalysts that allow obtaining SPA and OSPA with a higher yield during the initial use in liquid-phase aerobic oxidation of naphthene-paraffinic hydrocarbons were reused in the oxidation of naphthene-paraffinic hydrocarbons. The reaction conditions are the same as in initial use during reuse of catalysts in liquid-phase aerobic oxidation process of naphthene-paraffinic hydrocarbons

**Table 8. Liquid-phase aerobic oxidation of naphthene-paraffinic hydrocarbons: a)  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> modified with 10% and 20% Mn salt; b) reuse of bimetallic modified  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with 10% and 20% Mn and Cr salts as a catalyst**

Catalyst	Oxidate		Obtained products					
	Acid number, mgKOH/g	Yield, %	SPA		OSPA		SPA+OSPA, %	Non-saponifiable matter
			Acid number, mgKOH/g	Yield, %	Acid number, mgKOH/g	Yield, %		
a) $\gamma$ -Al <sub>2</sub> O <sub>3</sub> modified with 10% and 20% Mn salt								
$\gamma$ -Al <sub>2</sub> O <sub>3</sub> (MEA) mod. with 10% Mn	52.0	97.0	140.0	6.7	130.0	11.7	28.4	71.6
$\gamma$ -Al <sub>2</sub> O <sub>3</sub> (MEA) mod. with 20% Mn	49.2	97.6	160.0	17.7	110.0	14.2	31.9	68.1
$\gamma$ -Al <sub>2</sub> O <sub>3</sub> (DEA) mod. with 10% Mn	55.0	97.4	124.0	21.5	120.0	15.0	36.5	63.6
$\gamma$ -Al <sub>2</sub> O <sub>3</sub> (DEA) mod. with 20% Mn	58.0	98.0	125.0	24.6	100.0	14.0	38.6	61.4
b) $\gamma$ -Al <sub>2</sub> O <sub>3</sub> (bimetallic) modified with 10% and 20% Mn and Cr salts								
10% (Mn:Cr = 1:3) $\gamma$ -Al <sub>2</sub> O <sub>3</sub> (MEA)	54.0	97.0	112.0	19.0	119.0	15.7	34.7	65.3
20% (Mn:Cr = 1:3) $\gamma$ -Al <sub>2</sub> O <sub>3</sub> (MEA)	56.0	96.0	150.0	21.5	120.7	16.7	38.2	61.8
10% (Mn:Cr = 1:3) $\gamma$ -Al <sub>2</sub> O <sub>3</sub> (DEA)	55.0	97.2	139.2	24.4	123.6	16.4	40.8	59.2
20% (Mn:Cr = 1:3) $\gamma$ -Al <sub>2</sub> O <sub>3</sub> (DEA)	59.0	97.6	40.0	26.0	126.2	19.2	45.2	54.8

When we look through the yield of SPA+OSPA obtained by the oxidation of naphthene-paraffinic hydrocarbons by the reuse of the catalysts given in Table 8 (a) –  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (MEA) modified with 10% and 20% Mn salt and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (DEA) modified with 10% and 20% Mn salt, it becomes clear, that a mixture of synthetic organic acids is synthesized with lower yield - ~2-2.2% by the initial use of these catalysts. And it's considered a satisfactory result. As can be seen from Table 8, (bimetallic) modified  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts (b) show high catalytic activity even when reused. A small decrease - ~1-1.6% occurs in the yield of the mixture of acids by the reuse of these catalysts.

### **Study of the formal kinetic regularities of the time dependence of the liquid-phase catalytic oxidation process of naphthene-paraffinic hydrocarbons**

The time dependence of the changes in liquid-phase aerobic oxidation process of naphthene-paraffinic hydrocarbons in the presence of catalysts based on nano  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was studied by analyzing the IR spectra of the samples taken at one-hour intervals.

In the presence of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (DEA) catalyst modified with 20% Mn salt, an absorption band at 1708 cm<sup>-1</sup> characteristic for C=O bond is observed in the IR spectrum of the sample taken one hour after the start of the reaction. The IR spectra of the samples taken at 1, 3 and 4 hours of oxidation are practically identical. However, the intensity of the absorption band corresponding to C=O bond of carbonyl group increased. Further oxidation of the mixture of naphthene-paraffinic hydrocarbons revealed that intensity of the absorption band at 1715 cm<sup>-1</sup> (C=O) continued to increase after 6 hours of oxidation in the IR spectrum.

Depending on the duration of the oxidation process, the change in the optical density of C=O bond formed in the process is presented in Table 9.

Thus, IR spectroscopic analysis of the oxidation reaction of the naphthen-paraffinic fraction in the presence of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-based catalysts proved that the result in the 5th and 6th hours of the

oxidation reaction is almost the same, so the reaction should be carried out for 5 hours.

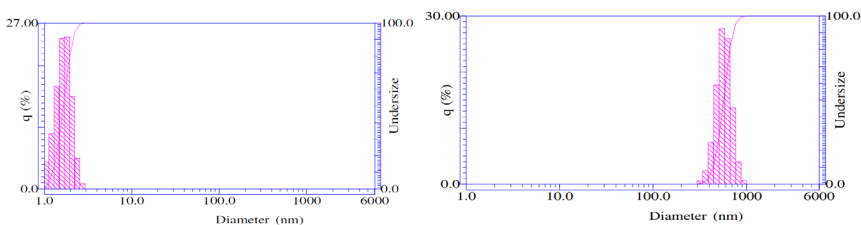
**Table 9. Changes in the optical densities of D<sub>968</sub>(CH), D<sub>1028</sub>(CH), D<sub>1708</sub>(C=O), D<sub>1762</sub>(OH) in the taken samples according to the time of the oxidation process**

Sample	D <sub>968</sub> (CH)	D <sub>1028</sub> (CH)	D <sub>1708</sub> (C=O)	D <sub>1762</sub> (C=O)
Sample	0.002	0.002	-	-
The 1 <sup>st</sup> hour	0.001	0.002	0.004	-
The 2 <sup>nd</sup> hour	0.001	0.001	0.008	-
The 3 <sup>rd</sup> hour	0.001	0.001	0.022	-
The 4 <sup>th</sup> hour	0.002	0.001	0.026	-
The 5 <sup>th</sup> hour	0.001	0.002	0.037	-
The 6 <sup>th</sup> hour	0.001	0.001	0.041	0.023

### Determination of particle sizes in systems consisting of nano $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts modified with Mn, Cr, Co metal salts

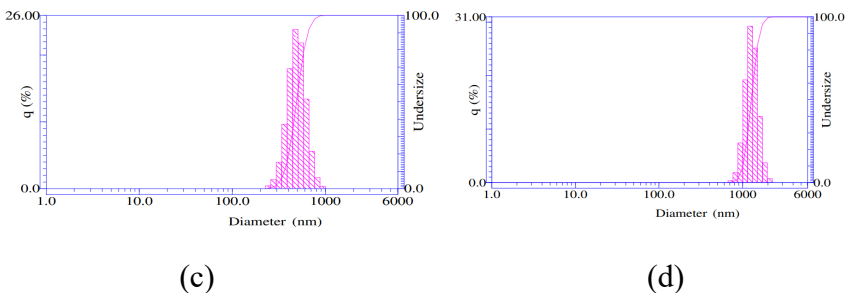
Dynamic light scattering (DLS) method was applied using an LB 550 (Horiba, Japan) analyzer at 23.3°C to determine the size and distribution of nano  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> crystals modified with variable valence metal salts studied as catalysts in the oxidation process of naphthene-paraffinic hydrocarbons.

DLS parameters differ significantly before the process, after 1 hour and after 5 hours during catalytic oxidation of naphthene-paraffinic hydrocarbons in the presence of nano- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (MEA) modified with Mn salt at 20% mas. (Fig. 3).



(a)

(b)



**Figure 3. DLS spectrum of naphthene-paraffinic hydrocarbons (a), NPH and catalyst mixture, catalytic powder in liquid phase -  $\gamma$ - $\text{Al}_2\text{O}_3$  modified with 20% Mn ( MEA) before (b), after 1 hour (c) and after 5 hours (d) of the oxidation process**

Thus, according to DLS spectrum of the catalytic powder in the liquid phase after 1 hour - c) and 5 hours after - d) the oxidation process: c) distribution of particles from 0 nm to 481.6 nm is not observed. The average value was 487.4 nm, the maximum value was recorded at 489.3 nm. No particle distribution is observed from 489.3 nm to 6000 nm; d) distribution of particles from 0 nm to 1248.8 nm was not observed and the average value was 1270.0 nm and the maximum value was recorded at 1270.9 nm. The distribution of particles from 1270.9 nm to 6000 nm is not observed.

During the oxidation process in the presence of nano- $\gamma$ - $\text{Al}_2\text{O}_3$  (MEA) modified with Mn salt in the amount of 20% mas., while the average value of the particle size after 1 hour of the reaction was  $\sim 0.5 \mu\text{m}$ , at the 5th hour of the reaction, this value was  $1.2 \mu\text{m}$ . This difference may be related to the influence of the reaction medium on the oxidation process of hydrocarbons. Thus, the catalyst forms a dispersed system of micro-sized particles in the liquid phase consisting of naphthene-paraffinic concentrate, the size of the particles increases by 2.4 times after the reaction. The formation of poorly aggregated particles of the catalyst in the reaction medium can be explained by the fact that they are surrounded by reaction products.

## Synthesis of nitrogen derivatives of synthetic petroleum acids and study of obtained compounds as inhibitors against CO<sub>2</sub> corrosion of steel

Aminoesters were synthesized on the basis of SPA and ethanolamines (monoethanolamine (MEA), diethanolamine (DEA) and triethanolamine (TEA)) obtained as a result of the oxidation process. "ACM Instruments Gill AC No. 1197" model device ("ACM Instruments Version 5" program) was used to study the effect of synthesized aminoesters on the kinetics of CO<sub>2</sub> corrosion. Effect of the obtained aminoesters on the corrosion kinetics of steel was studied in a 1% solution of NaCl in water saturated with CO<sub>2</sub>.

**Table 10. Long-term use of aminoesters obtained on the basis of SPA:DEA and SPA:MEA at a concentration of 100 mg/l as a corrosion inhibitor**

Inhibitor	Duration, time	Corrosion current, mA/m <sup>2</sup>	Corrosion rate, mm/il	Metal loss, mm	Corrosion protection effect, %
Inhibitor-free	100	3353.3	3.8865	0.0466478	-
	200	2884.2	3.3428	0.086301	-
	300	3205.4	3.715	0.1287844	-
	370	2778.5	3.2202	0.1557425	-
	400	3037.1	3.52	0.1697305	-
	430.37	3114.5	3.6097	0.1812434	-
	433.37	1358.6	1.5747	0.1819728	-
SPA:MEA-based aminoester	100	101.88	0.1180865	0.001315	97
	200	97.169	0.1126191	0.002778	97
	300	77.802	0.0901728	0.00397	97
	370	82.99	0.096186	0.004933	97
	400	91.018	0.1054903	0.005288	97

**Cont. of Tab. 10**

	430.37	96.142	0.1114297	0.005691	97
	433.37	92.165	0.0720501	0.00572	95
SPA:DEA- based aminoester	100	150.56	0.130447	0.001076	96.6
	200	200.9	0.124979	0.006726	96.3
	300	587.2	0.102533	0.016652	97.2
	370	820.89	0.108546	0.025552	96.63
	400	1203.5	0.11785	0.030948	96.65
	430.37	1437.6	0.12379	0.03757	96.57
	433.37	1776.6	0.08441	0.04354	94.64

Among the synthesized aminoesters, the aminoester obtained on the basis of SPA and MEA at a concentration of 100 mg/l had the maximum corrosion protection effect (99.54%) in 20 hours. For the purpose of studying the long-term effect of compounds as inhibitors against carbon dioxide corrosion, the effect of compounds with a higher protective effect in 20-hour results on the corrosion process for ~433 hours (18 days) was also studied (Table 10).

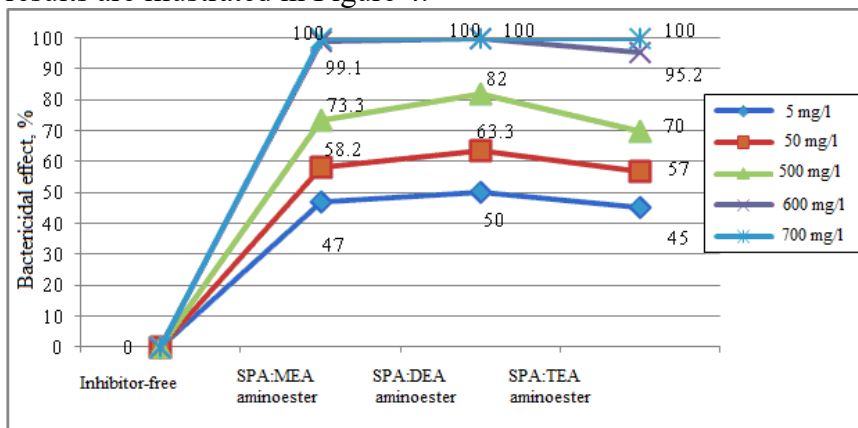
High results were obtained during the use of organic acid complexes as inhibitors against corrosion, in this regard, the long-term effect of HCOOH (G II) and CH<sub>3</sub>COOH (G I) complexes of imidazoline derivatives obtained on the basis of synthesized SPA and polyethylenepolyamines against CO<sub>2</sub> corrosion was studied. According to the results of the effect of G-I and G-II complexes taken at a concentration of 100 mg/l on steel corrosion during 100-433 hours, G-I showed 95.5%, G-II - ~97% of protective effect on the 18th day (at 433.37 hours) of the experiment (Figure 4, 5).

Thus, aminoesters obtained on the basis of SPA and ethanolamines; mixture of OSPA with SPA and complexes of imidazolines with organic acids on the basis of polyethylenepolyamine can be used as effective corrosion inhibitors in CO<sub>2</sub> medium.



## Study of bactericidal-inhibitory properties of nitrogenous derivatives of synthetic petroleum acids

Effect of bactericidal effect of aminoesters obtained on the basis of SPA and metal (Ba, Al) salts of SPA, synthesized in the presence of  $\gamma\text{-Al}_2\text{O}_3$ -based catalysts, on the life activity of SRB for 15 days was considered. *Desulfovibrio desulfuricans* strain 1143 taken from the Absheron-Binagadi field based on “ГОСТ 39-151-83” was used as a research object to study the bactericidal effect of the synthesized compounds. GOST 18963-73 was used to determine the bactericidal properties of the inhibitors. *Postgate B* nutrient medium was taken for the development of SRBs. It was taken to ensure that the pH of the medium was in the range of  $\sim 7\text{-}7.5$ . The results are illustrated in Figure 4.



**Figure 4. Graphic representation of bactericidal effect of aminoesters of SPA**

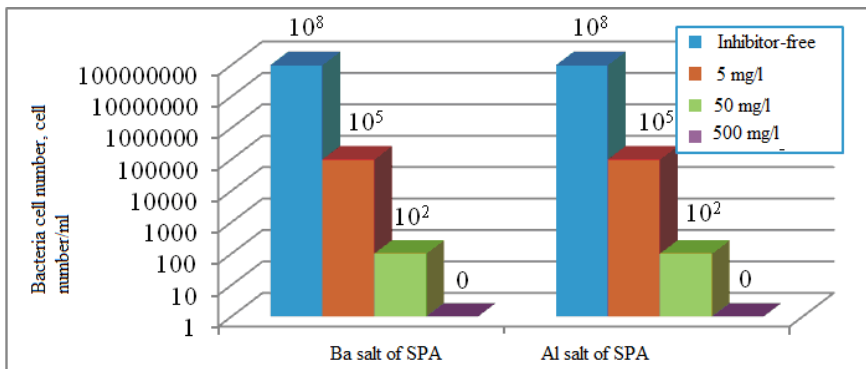
Simultaneously, Ba and Al salts of SPA were synthesized and the test results (10% hexane solution of each) as bactericide against SRB for 15 days are given in Table 11 and Figure 5.

As is evident from Table 11, Ba salt of SPA showed 53.3%, 80% and 100% bactericidal effect against SRBs at concentrations of 5, 50 and 500 mg/l, respectively; Al salt of SPA showed 55%, 85% and 100% bactericidal effect and completely stopped the development of SRBs.

**Table 11. Test results of metal (Ba and Al) salts of SPA as bactericides against SRB**

Metal salts of SPA	Conc. of substance, mg/l	Bacteria number (cell number/ml)	H <sub>2</sub> S amount mg/l	Bactericidal effect, Z-%
Ba salt of SPA	5	10 <sup>5</sup>	238	53,3
	50	10 <sup>2</sup>	102	80
	500	-	-	100
Al salt of SPA	5	10 <sup>5</sup>	230	55
	50	10 <sup>2</sup>	76.5	85
	500	-	-	100
Control-I	-	-	24	-
Control-II	-	-	510	-
Control-III	-	10 <sup>8</sup>	-	-

Note: Control-I amount of H<sub>2</sub>S in SRB-free medium, Control-II amount of H<sub>2</sub>S in medium with SRB, Control-III Number of bacteria in nutrient medium



**Figure 5. Graphic representation of the bactericidal effect of Ba and Al salts of SPA on the cell number of SRB**

According to Figure 5, it can be concluded that although the number of bacterial cells in inhibitor-free medium is hundreds of millions (10<sup>8</sup>), the number of bacterial cells in the medium with 500 mg/l inhibitor has decreased from one hundred million to zero.

Thus, application of synthesized SPA and OSPA in various fields has shown that the mixture of synthetic petroleum acids

obtained in the presence of  $\gamma\text{-Al}_2\text{O}_3$  catalysts modified with variable valence metal salts are indeed industrially important compounds with a wide field of application, and those inhibitors may be recommended for industrial application. Simultaneously, synthetic petroleum acid mixtures are currently the best substitutes for natural petroleum acids which are in short supply.

## CONCLUSIONS

1. Liquid-phase aerobic oxidation process of naphthene-paraffinic hydrocarbons separated from the diesel fraction of the Azerbaijani petroleum mixture boiling at 190-330°C was carried out in the catalytic presence of  $\gamma\text{-Al}_2\text{O}_3$  modified with salts of variable valence metals (Mn, Co, Cr). MEA and DEA were used as stabilizers for the sol-gel synthesis of  $\gamma\text{-Al}_2\text{O}_3$ , which plays the role of a carrier in catalysts. The yield of SPA+OSPA was higher (with a yield of 38.7% when catalyst is taken 0.2% mas. according to raw material) during the oxidation process carried out in the presence of  $\gamma\text{-Al}_2\text{O}_3$  (DEA) modified with 10% Mn salt as a catalyst in monometallic catalytic systems [1, 2, 3, 4, 5, 6].
2. As the mass fraction of metal in  $\gamma\text{-Al}_2\text{O}_3$  modified with metal salts increased, a mixture of synthetic organic acids was obtained with a higher yield. Thus, by an increase in the content of Mn in  $\gamma\text{-Al}_2\text{O}_3$  (DEA) modified with Mn salt increased from 10% to 20%, SPA+OSPA mixture was obtained with a yield of 40.6%. Also, the yield of the target products increased slightly when a 1:3 mechanical mixture of  $\gamma\text{-Al}_2\text{O}_3$  (DEA) modified with two different metal salts was used as a catalyst in the process –  $\gamma\text{-Al}_2\text{O}_3$  (DEA) modified with 20% Mn salt / in the catalytic use of  $\gamma\text{-Al}_2\text{O}_3$  (DEA) = 1/3 mechanical mixture modified with 20% Cr salt, the yield of synthetic organic acids mixture was 44.4% [8, 10, 11, 12, 15].
3. Bimetallic modifications of  $\gamma\text{-Al}_2\text{O}_3$  with Mn, Co, Cr salts were used as a catalyst in the oxidation process of dearomatized diesel fraction. Thus, in bimetallic catalysts used in liquid-

phase oxidation of naphthene-paraffinic hydrocarbons with air oxygen, a higher yield of SPA and OSPA was achieved: 1) SPA with 22% yield and OSPA with 17.2% yield were obtained in the presence of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> bimetallic catalyst (MEA was used as a stabilizer in the synthesis) modified with 20% (Mn:Cr=1:3); SPA with 26.8% yield and OSPA with 20% yield were obtained (DEA was used as a stabilizer in the synthesis) in the presence of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> modified with 20% (Mn:Cr=1:3).

4. Simultaneously, catalysts were reused in the oxidation process, and a mixture of synthetic organic acids was synthesized in the presence of monometallic modifications of transition metal salts with  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> - ~2% less yield than the initial use, and ~1-1.6% less yield in bimetallic modifications.
5. For the purpose of determining the optimal parameters of the oxidation process, a catalytic composition nano  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (MEA) and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (DEA) carrier modified with 20% Mn salt was taken, and the time dependence of the oxidation process of naphthene-paraffinic hydrocarbons was determined by IR spectroscopy, the size and distribution of catalyst particles were determined using DLS method.
6. The corrosion protection property of aminoesters obtained on the basis of SPA and ethanolamines (MEA, DEA and TEA) was studied: for 20 hours steel electrode at concentrations of 50 and 100 mg/l, respectively, SPA:MEA aminoester - 93.2 and 99.5%, SPA:DEA aminoester provided 83.2 and 99.3% corrosion protection, while SPA:TEA aminoester showed 82.8 and 99.3% corrosion protection. Complexes of imidazoline derivatives obtained on the basis of SPA and OSPA with organic acids (CH<sub>3</sub>COOH, HCOOH) were developed, and the effect of both imidazoline derivatives complexes and aminoesters against CO<sub>2</sub> corrosion was studied in 18-19 days. Thus, at a concentration of 100 mg/l, CH<sub>3</sub>COOH complex of imidazoline had 95.5% of corrosion protection effect on the 18th day (433.37 hours), HCOOH complex - ~97%, the aminoester obtained on the basis of SPA:MEA - 95%, and the aminoester obtained on the basis of SPA:DEA - 94.6%. The

use of synthesized compounds as effective corrosion inhibitors has been recommended [7, 16, 17].

7. Effect of Ba and Al salts of SPA, as well as aminoesters, on the life activity of SRBs was studied as a bactericide-inhibitor in the process of biological corrosion. It was determined that Ba and Al salts of SPA at a concentration of 500 mg/l, and each of the aminoesters at a concentration of 700 mg/l showed 100% bactericidal effect [9, 13].

**The main content of the dissertation work was presented in the following publications:**

1. Afandiyeva, L.M. Catalytic oxidation of the naphthene-paraffinic petroleum fraction in the presence of  $\gamma\text{-Al}_2\text{O}_3$  modified with Cr-, Co- Mn- salts / L.M. Afandiyeva, H.J. Ibrahimov, G.Y. Rustamli, S.F. Ahmadbayova, Kh.R. Mammadova, B.M.Aliyev, V.M.Abbasov // Chemistry problems, - Baku: - 2019. No. 2 (17), - p.323-329.
2. Rustamli, G.Y. Oxidation of naphthene-paraffinic hydrocarbons separated from the diesel fraction of oil on nano  $\gamma\text{-Al}_2\text{O}_3$  by CVD method in the presence of catalytic systems with transition metals in the liquid phase // "1st Republican scientific conferences of students" dedicated to the National Leader Haydar Aliyev's 96th anniversary of the birth, Baku Higher Oil School, Baku: April 15-19, 2019, p. 24-25.
3. Abbasov, V.M., Afandiyeva, L.M., Rustamli, G.Y., Mammadova, Kh.R., Nasibova, G.G., Ahmadbayova, S.F., Ibrahimov, H.J. Oxidation of petroleum hydrocarbons in the catalytic participation of  $\gamma\text{-Al}_2\text{O}_3$  modified with air oxygen and Cr-, Co-, Mn- salts // "Actual problems of modern natural and economic sciences" International scientific conference - Part I, - Ganja: - May 3-4, -2019, -p.193-194.
4. Abbasov, V.M., Afandiyeva, L.M., Rustamli, G.Y., Ahmadbayova, S.F., Ibrahimov, H.C. Synthesis of synthetic petroleum acids based on naphthene-paraffin hydrocarbons in the catalytic presence of nano  $\gamma\text{-Al}_2\text{O}_3$  modified by Cr-, Co-, Mn- salts // "Kimyanın yıldızlı 100. yılı Ulusal Kimya Kongresi", Yıldız Teknik universiteti, - İstanbul: -10-13 Eylül, -2019, - p.270.
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- anniversary of academician Y.H. Mammadaliyev Institute of Petrochemical Processes Baku: October 2-4, 2019, p.150.
6. Abbasov, V.M. Aerobic oxidation of naphthene-paraffinic hydrocarbons of petroleum in the presence of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> modified by transition metals / V.M. Abbasov, L.I. Aliyeva, L.M. Afandiyeva, H.J. Ibrahimov, G.Y. Rustamli // Processes of Petrochemistry and Oil Refining, -Baku: -2020. Vol. 21, № 1, - p.80-89.
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  9. Afandiyeva, L.M. Study of bactericidal-inhibitory properties of aminoesters obtained on the basis of synthetic petroleum acids / L.M. Afandiyeva, D.B. Agamaliyeva, G.Yu. Rustamli, N.N. Babanly, G.G. Nasibova, S.F. Ahmadbayova, V.M. Abbasov // Neftepererabotka i neftekhimiya, - Russia: - 2020. No. 8, -p. 13-16.
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12. Ibrahimov, H.J. Synthesis and physical and chemical properties of nanodispersed aluminum oxide / H.J. Ibrahimov, G.Yu. Rustamli, S.R. Melikli, Y.G. Yusifov, Z.M.Ibrahimova, L.M.Afandiyeva, M.I. Rustamov, L.M. Saadova // Reports of the National Academy of Sciences of Azerbaijan, Azerbaijan, - Baku:-2020. v. LXXVI, No. 3-4, p.34-40.
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  14. Rustamli, G.Y. Study of the process of liquid-phase catalytic oxidation of naphthene-paraffinic hydrocarbons // - Nakhchivan: Azerbaijan National Academy of Sciences, Scientific works, -2021. Vol. 2, No. 17, - p. 36-42.
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  16. Abbasov, V.M. Study of aminoesters of synthetic petroleum acid obtained by aerobic oxidation of naphthene-paraffinic hydrocarbons as corrosion inhibitors / V.M. Abbasov, L.M. Afandiyeva, D.B. Agamaliyeva, G.Yu. Rustamli, R.M. Yusifov, Ch.E. Agayev // Practice of Anti-Corrosion Protection, - 2022. No. 3 (27), - p. 47-56.
  17. Abbasov, V.M., Afandiyeva, L.M., Agamaliyeva, D.B., Rustamli, G.Y., Agayev, C.E. Study of aminoesters obtained on the basis of synthetic petroleum acids as corrosion inhibitors



// Republican scientific conference "Catalysts, olefin-based oils" dedicated to the 90th anniversary of Academician Nadir Mir-Ibrahim oglu Seyidov, - Baku: - May 19-20, - 2022, - p.55.

A handwritten signature in blue ink, appearing to be 'Mir-Ibrahim', is written in a cursive style.



The defense will be held on 22<sup>nd</sup> December 2023 at 10<sup>00</sup> at the meeting of the One-time Dissertation council BFD 1.16 on the base of Dissertation council ED 1.16 of Supreme Attestation Commission under the President of the Republic of Azerbaijan operating at academician Y.H. Mammadaliyev Institute of Petrochemical Processes of the Ministry of Science and Education.

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