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ABSTRACT

of the dissertation for the degree of
Doctor of Philosophy

ACYLATION REACTIONS OF *p*-CYCLOALKYLPHENOLS WITH ACETIC ACID, BENZOYL AND ACETYL CHLORIDES IN THE DISPERSION $ZnCl_2/Al_2O_3$ CATALYTIC SYSTEM

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The work was performed of the "Chemistry and technology of alkylphenols" laboratory of academician Y.H. Mammadaliyev Institute of Ministry of Science and Education Republic of Azerbaijan.

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GENERAL CHARACTERISTICS OF THE WORK

Relevance of the topic and degree of elaboration. The countries with a strong economy are more interested in the improvement of qualitative properties of fuels, oils, polymer materials and rubber than their production. Therefore, a noticeable increase is observed in production of antioxidants, additives, stabilizers, plasticizers and other chemical additives added to them. Alkylphenol-based compounds have a special place among these chemical additives. It's no coincidence that more than 70% of currently-used chemical additives are alkylphenol-based chemical additives. The most effective and important advantage of these chemical additives is their resistance to high temperatures, not changing the color of the polymer, resistance to the effects of light, air oxygen, aggressive environment and non-toxicity[1]. Alkylphenols are applied for preven-ting spoilage of food products and as stabilizers for polymers used in the preparation of children toys. Currently, the demand for alkylphenols in the world is 0.5 mln. ton. Almost 80-85% of this demand is met by various manufacturers. But despite this, the demand for alkylphenols increases by 2% every year. It's caused by new application fields for alkylphenols. Recently, alkylphenols have been used as ligands for catalytic precursors used in ethylene oligomerization and polymerization processes, as antiradiation agents for increasing radiation resistance of polymers, in the production of pure oxygen widely used in medicine, as an insecticide, pesticide against plant pests and diseases in agriculture, and intestinal bacteria of large and small horned animals. They are widely used as bactericides and disinfectants against microbes. Besides, currently-used alkylphenol-containing chemical additives do not meet the ever-increasing demand of the industry.

Thus, known alkylphenol-based chemical additives are not fully soluble in the objects they are used in, are not thermally stable, have environmental and technological problems, etc. In this regard, aceto- and benzophenones-containing polyfunctional chemical additives are

[1] Расулов Ч.К., Агамалиев З.З., Гасанова Г.Д., Нагиева М.В. Синтез алкилфенолов и применение их в реакциях аминометилирования. Баку: Муаллим, – 2021, – 197 с.

of interest[2].

The dissertation work is dedicated to the current problem - the study of acylation reactions of *para*-cycloalkylphenols with acetyl chloride, benzoyl chloride and acetic acid using $ZnCl_2$, dispersed $ZnCl_2$-impregnated γ-Al_2O_3 and KU-23 catalysts and determining the application areas for the obtained products.

The object and subject of the study. The object of the studies is the acylation reactions of *para*-methylcycloalkylphenols with acetyl chloride, benzoyl chloride and acetic acid, selection of effective catalysts; and the subject is determining the efficient use fields of synthesized cycloalkylaceto- and benzophenones.

Research goals and objectives. The main goal of the study is obtaining cycloalkylaceto- and benzophenones by the interaction reactions of *para*-cycloalkylphenols (synthesized by catalytic cycloalkylation reactions of phenol with methylcycloalkenes of different structures) with acetyl chloride, benzoyl chloride, and acetic acid using various catalysts - $ZnCl_2$, dispersed $ZnCl_2$ impregnated γ-Al_2O_3, KU-23 and testing them as an antioxidants for diesel fuel, stabilizers in polymer materials, and radiation-resistant antirads.

The following studies were carried out to achieve the goal:

- interaction reactions of *para*-(1-methylcyclopentyl)-, *para*-[1(3)-methylcyclohexyl]-, cyclodimers of isoprene based *para*-cycloalkylphenols with acetyl chloride in the presence of $ZnCl_2$, $ZnCl_2$ impregnated γ-Al_2O_3 and KU-23 catalysts;
- interaction reactions of cycloalkylphenols with benzoyl chloride in the presence of dispersed $ZnCl_2$ impregnated γ-Al_2O_3 catalyst;
- acylation reactions of cycloalkylphenols with acetic acid in the presence of dispersed $ZnCl_2$ impregnated γ-Al_2O_3 catalyst;
- test of the synthesized target products as an antioxidant for diesel

[2] Haydarli, G.Z. Synthesis of 2-hydroxy-3[3(4)-methylcyclohexen-3-yl-isopropyl]-5-methylacetophenones / G.Z.Haydarli, M.V.Nagiyeva, Z.Z.Agamaliev [etc.] / / Chemistry and chemical technology, – Ivanovo: – 2022. v.65, issue 3 – p. 100-106.

fuel, a stabilizer for high-pressure polyethylene, and antiradiation agent.

Research methods. Catalytic acylation reactions of *para*-cycloalkylphenols with acetyl chloride, benzoyl chloride and acetic acid were carried out in a batch unit under laboratory conditions.

Main provisions for defence. Acylation reactions of *para*-cycloalkylphenols with acetyl chloride, benzoyl chloride and acetic acid were studied using $ZnCl_2$, γ $ZnCl_2$ impregnated γ-Al_2O_3 and KU-23 catalysts; the obtained cycloalkylaceto- and benzophenones were tested as antioxidants for diesel fuel, as stabilizers for polyethylene, and as antirads against radiation.

Scientific novelty of the research. For the first time, acylation reactions of para-(1-methylcyclopentyl)-, para-[1(3)-methylcyclohexyl]-, para-[3(4)-methylcyclohexen-3-yl-isopropyl]phenols with acetyl chloride in the presence of in the presence of $ZnCl_2$, dispersed¬$ZnCl_2$-impregnated γ-Al_2O_3 and KU-23 catalysts, with benzoyl chloride and acetic acid in the presence of a dispersed $ZnCl_2$/γ-Al_2O_3 were systematically studied.

The effect of various kinetic parameters on the yield and selectivity of cycloalkylaceto- and benzophenones which obtained from the acylation reactions of para-cycloalkylphenols was studied.

The obtained cycloalkylaceto- and benzophenones were tested as antioxidants in diesel fuel, as stabilizers in polyethylene, and as antirads against radiation. 2 Azerbaijani patents were obtained based on the results obtained from scientific research.

Theoretical and practical significance of the research. A preliminary theoretical idea was formed on the effective properties of chemical compounds containing cycloalkyl, hydroxyl, aromatic ring, carbonyl groups as a result of the complex analysis and scientific justification of the researches. 2-Hydroxy-5-methylcycloalkylacetophenones were tested as antioxidants for diesel fuel, stabilizers in polyethylene, and antirads against radiation. The positive results of the tests allow recommend them for extensive testing.

Personal involvement of the author. All the results reflected in the dissertation were obtained by the author's direct participation in

the studies. Setting the issues, conducting experiments and preliminary tests, systematization, research and generalization of obtained experimental and scientific results were carried out with the participation of the author.

Approval and application. 25 scientific works have been published, including 2 Azerbaijani patents, 10 papers (6 of them abroad) and abstracts of reports at 13 international and republic level conferences.

The results of the dissertation were reported and discussed at the following conferences: International scientific conference of students, postgraduates and young scientists "Lomonosov-2021" (Moscow, 2021); the XVII International scientific-practical conference "New Polymer Composite Materials. Mikitayev Readings" (Nalchik, 2021, 2022, 2023); the 7th International Conference "Ecological and Environmental Chemistry-2022" (Kshinyov, 2022); the Republican scientific conference on "Actual Problems of the Chemistry of Heteroatomic Compounds" (Baku, 2022); Republican conference on "Environmental protection: Industrial and Household Waste Recycling" (Ganja, 2022); 4th International Conference on Innovations in Natural Science and Engineering (Baku, 2022), 6th International Turkish World Conference on Chemical Sciences and Technologies (Baku, 2022); "Baltic Chemistry Conference" (Gdansk, 2023); the IX International Russian-Kazakhstan scientific-practical conference "Chemical Technologies of Functional Materials" (Novosibirsk, 2023); scientific and technical conference "Radiation Safety: Regional Aspects" dedicated to academician Mahmud Karimov's 75th anniversary of birth (Nakhchivan, 2023); the conference "Synthesis and Study of Metal Complex and Metal-Organic Catalysis, (Co)Oligomer, (Co)Polymers" dedicated to academician Akif Azizov's 80th anniversary of birth (Baku, 2023).

The dissertation work was performed in the laboratory "Chemistry and Technology of Alkylphenols" at academician Y.H. Mammadaliyev Institute of Petrochemical Processes of the Ministry of Science and Education of the Republic of Azerbaijan.

The total volume of the dissertation, indicating the volume of the structural sections separately. The dissertation consists of 179 pages

of introduction (9819), 5 chapters (chapter I – 44454 characters, chapter II – 9294 characters, chapter III – 68161 characters, chapter IV – 52990 characters, chapter V - 8281 characters), conclusions (2895 marks), 159 literature sources, including descriptions of abbreviation-the total volume consists of 195894 characters (excluding pictures, tables, graphs, appendices and bibliography), The thesis includes 20 tables and 38 pictures.

Introduction describes and justifies the relevance, purpose, scientific novelty, theoretical and practical significance of the research, personal involvement of the author.

The first chapter deals with the literature review and analysis of the literature sources on obtaining of aceto- and benzophenones by acylation reactions of alkyl- and cycloalkylphenols in the presence of various catalysts according to the topic of the dissertation. Simultaneously, the known scientific researches in this field are critically analyzed and the scientific directions of the conducted scientific researches are justified.

The second chapter represents the experimental part. The initial raw materials, their physicochemical properties, elemental compositions, the course of experiments, description of the devices used, and the methods for the analysis of the target products obtained as a result of acylation reactions are given in the chapter. Simultaneously, it allows discuss the preparation method and analysis of the $ZnCl_2$ impregnated γ-Al_2O_3 used in acylation reactions.

The third chapter is dedicated to the study of the acylation reactions of *para*-cycloalkylphenols with acetyl chloride in the presence of $ZnCl_2$, γ-Al_2O_3 impregnated with dispersed $ZnCl_2$ and KU-23 catalysts, effect of kinetic parameters on the yield and selectivity of the target products.

The fourth chapter describes the study of acylation reactions of *para*-cycloalkylphenols with benzoyl chloride and acetic acid in the presence of γ-Al_2O_3 impregnated with dispersed $ZnCl_2$ catalyst, and effect of various kinetic parameters on the yield and selectivity of the obtained products.

The fifth chapter introduces the tests results of cycloalkylaceto-

and benzophenones obtained by the acylation reactions of *para*-cycloalkylphenols as antioxidants in diesel fuel, antirad against radiation and thermostabilizers for polyethylene.

The dissertation concludes with a summary of the work, conclusions, references, a list of additions and abbreviations.

MAIN CONTENTS OF THE WORK

Primary raw materials, catalysts, conduction of experiments and methods for analysis of reaction products

pra-[1(3)-Methylcyclohexyl]phenols, *para*-(1-methylcyclopentyl)phenol, 1-methyl-3-isopropenylcyclohexen-1 (diprene), 1-methyl-4-isopropenylcyclohexen-1 (dipentene) *para*-cycloalkylphenols obtained on the basis of, mixture of isoprene cyclodimers (160-180°C fraction), *para*-arylalkylphenol were used in the studies.

para-(1-Methylcyclopentyl)phenol is obtained by the interaction of [p-(1-MCP)F] 1-methylcyclopentene with phenol in the presence of KU-23, Seokar-2, orthophosphoric acid-treated Seolite-Y catalysts. [p-(1-MCP)P] has the following physicochemical properties: $T_{b.}$=147-148°C (10 mm Hg), Tm=88°C, mol. mass – 176.

para-(1-Methylcyclohexyl)phenol is obtained by the interaction of [p-(1-MCH)P] 1-methylcyclohexene with phenol in the presence of KU-23, Zeokar-2, orthophosphoric acid-treated Seolite-Y catalyst. Physicochemical properties of [p-(1-MCP)P]: $T_{b.}$=161-164°C (10 mm Hg), Tm = 96°C, mol. mass – 190.

para-(3-Methylcyclohexyl)phenol is obtained by the interaction reactions of [p-(3-MCH)P] 3-methylcyclohexene and phenol in the presence of KU-23 and orthophosphoric acid-treated Seolite-Y catalysts. Physicochemical properties of [p-(3-MCH)P]: $T_{b.}$=158-160°C (10 mm Hg), Tm = 91°C, mol. mass – 190.

Diprene (DP)-based *para*-cycloalkylphenol is obtained by the alkylation of phenol with diprene in the presence of KU-23 and orthophosphoric acid-impregnated Seolite-Y catalysts and possesses the following physicochemical properties: $T_{b.}$ = 193-196°C (10 mm Hg), T_m= 106°C, mol. mass – 230.

Dipentene (DPT)-based *para*-cycloalkylphenol is obtained by the alkylation of phenol with dipentene in the presence of KU-23 and orthophosphoric acid-impregnated Seolite-Y catalysts and has the following physicochemical properties: $T_{b.}$= 198-202°C (10 mm Hg), T_m = 107-108°C, mol. mass – 230.

Cyclodimers of isoprene (CDİ)-based *para*-cycloalkylphenol is obtained by the alkylation of phenol by CDİ in the presence of KU-23 and orthophosphoric acid-impregnated Seolite-Y catalysts and possesses the following physicochemical properties: $T_{b.}$ = 190-205°C, n_D^{20}=1.5450, ρ_4^{20}= 0.9145g/cm^3, mol. mass – 230.

p-Arylalkylphenol is obtained by the alkylation of liquid products obtained by the pyrolysis process of low-octane gasoline in the presence of a KH-30 catalyst with a fraction of 130-190°C and assessed for the following physicochemical properties: $T_{b.}$=160-180°C, n_D^{20}=1.5675, ρ_4^{20}= 0.9736 g/cm^3, mol. mass – 200.

Acetyl chloride – T_m = - 112°C, $T_{b.}$= 52°C, n_D^{20}=1.3710, mol. mass – 78.

Benzoyl chloride – T_m = -1°C, $T_{b.}$= 197.2°C, n_D^{20}= 1.5537, mol. mass– 141.

Acetic acid – $T_{b.}$= 16-17°C, $T_{b.}$= 118-119°C, n_D^{20}=1.3710, mol. mass– 60.

$ZnCl_2$, $ZnCl_2$ impregnated γ-Al_2O_3 and KU-23 catalysts were used in the acylation reactions of *para*-alkylphenols.

Anhydrous zinc chloride is a strong Lewis acid. Therefore, zinc chloride is widely used as a catalyst in acylation reactions.

KU-23 (modification 10/60 (GOST 20298)) pore radius – 250-600Å, contains up to 55-70% water, thermally stable up to 170°C. Therefore, KU-23 cationite is heated up to 110°C to get rid of water before use. During the acylation process, due to the influence of temperature, sulfogroups are removed from the catalyst and resin-like compounds are collected on the surface of the catalyst; as a result, the activity of the catalyst decreases. Unlike KU-2 catalyst, KU-23 is reactivated with 2-4% hydrochloric acid and is used again in acylation reactions.

The $ZnCl_2$ impregnated γ-Al_2O_3 catalyst is developed by the following method: at first, 40 g of Al_2O_3 are dried at 110ºC, then baked in a Muffle furnace at 500ºC during 3 h. Roasted 40 g of Al_2O3 is divided into four parts of 10 g each, and three parts of them are impregnated with $ZnCl_2$ salt of 5, 10, 20% in Al_2O_3, and one part of Al_2O_3 is kept free. The catalyst is dried in the Muffle furnace at 110ºC in air flow for 3 hours and baked at different temperatures - 800ºC for 5 h. The prepared $ZnCl_2/\gamma$-Al_2O_3 catalyst was studied in modern devices.

Chromatographic analysis of *para*-cycloalkylphenols used in acylation reactions was carried out in LXM-72 chromatograph.

“Plenatary Ball Mill PM-100” device, produced by "RETSCH" company (Germany) was used for granulation of $ZnCl_2$, applied as a catalyst in the reaction.

Sizes of $ZnCl_2$ salt used as a catalyst for acylation reactions in distilled water at different percentages were determined by dynamic light scattering analysis. The dynamic light scattering analysis was performed on LB-550 device manufactured by HORIBA company (Japan).

IR and NMR spectroscopy analysis methods were used to determine the structures of the primary and obtained products taken for the reaction.

The IR spectra of the products were recorded using an ALPHA IR-Fourier spectrometer of "BRUKER" (Germany) on a Se-Zn crystal, in the wavelength range of 600-4000 cm^{-1}.

NMR spectra were recorded using deuterated benzene at room temperature at a working frequency of 300.18 MHz in the Fourier spectrometer of the German company "BRUKER".

As the synthesized cycloalkylacetophenones and benzophenones are high-boiling compounds, the purity of these substances was determined by thin-layer chromatography.

The density (ρ) of the synthesized products was determined by the ASTM D5002 method on AntonPaar "DMA 4500M" device, the refractive index (n_D^{20}) was determined by the AntonPaar company "Abbemat 500" device using the refractometric method, and the Kinematic accuracy was determined with the SVM 3000 model of the "Stabinger viscometer" device of the Anton Paar company.

The elemental composition of the obtained cycloalkylaceto- and benzophenones was determined using the "Tru Spec® Micro" analyzer of the "Leco" company.

The thermal analysis of the catalyst were carried out in an inert medium using NETZSCH STA-449 F3 "Jupiter" thermoanalyzer.

Two contact methods were used to determine the dielectric parameters of the materials.

Acylation reactions of *p*-cycloalkylphenols with acetyl chloride in the presence of $ZnCl_2$ catalyst

Acylation reactions of *para*-(1-methylcyclopentyl)-, *para*-[1(3)-methylcyclohexyl], *para*-[3(4)-methylcyclohexen-3-yl-isopropyl]-, *para*-arylalkylphenols with acetyl chloride in presence of $ZnCl_2$ were studied catalyst at 120-160°C during 20-60 min, in 1:0.5÷3 mol ratios of phenol to acetyl chloride, and 16.5 g of the catalyst amount.

For example, the results of acylation reactions of *p*-(1-methylcyclohexyl)phenol with $ZnCl_2$ catalyst with acetyl chloride are given in Fig. 1.

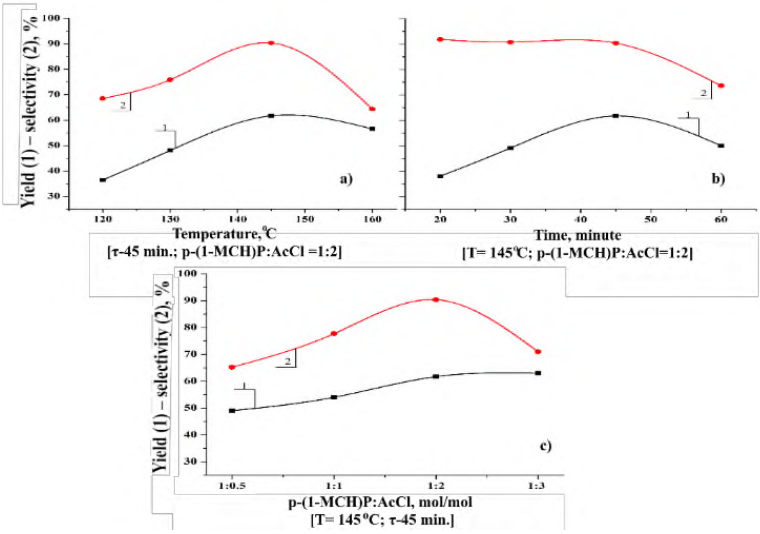


Fig. 1. The results of acylation reactions of para-(1-methylcyclohexyl)phenol with acetyl chloride in the presence of $ZnCl_2$ catalyst

As is evident from Fig. 1 (a), an increase in temperature from 120 to 145°C causes an increase in the yield of acetophenone from

36.4 to 61.7% (according to the taken cycloalkylphenol), and selectivity increases from 68.5 to 90.3%. Increase in the temperature up to 160°C causes a decrease in the yield of the target substance to 56.5%, and in selectivity to 64.3%. Decrease in yield and selectivity is explained by the increase in the kinetic energy of the molecules of the primary raw materials at high temperature and, as a result, obtaining other isomers. Therefore, increasing temperature above 145-150°C, such a positive result cannot be achieved; yield and selectivity decrease.

One of the most important factors affecting the yield and selectivity of the obtained target product is the process duration. The process time was studied within 20-60 min. As is evident from the figures, when the meeting time of the primary raw materials is 45 minutes, the yield of 2-hydroxy-5(1-methylcyclohexyl)acetophenone is 61.7% in comparison to the obtained *para*-(1-methylcyclohexyl)phenol, and selectivity is 90.3% according to the target product. Effective result cannot be achieved by increasing or decreasing the process time.

One of the factors influencing on the yield of the target product obtained as a result of the acylation reaction is the mol. ratio of the initial raw materials. It can be seen from the figure that the yield of the target product is 61.7% in 1:2 mol. ratio of *para*-(1-methylcyclohexyl)phenol to acetyl chloride, and the selectivity for the target product is 90.3%. It's possible to increase the yield of the target product by increasing the concentration of acetyl chloride in the mixture. However, it isn't economically efficient, and the process selectivity drops to 71% for the target product. It's explained by obtaining other isomers in the specified concentrations of the components.

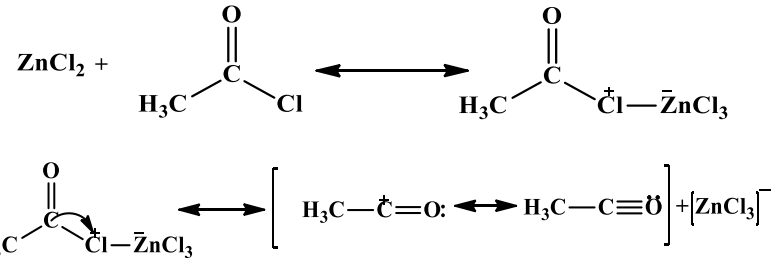
Thus, the following conditions were determined for the acylation reaction of *para*-(1-methylcyclohexyl)phenol with acetyl chloride in the presence of $ZnCl_2$ catalyst: reaction temperature − 145°C, duration 30 min, when *p*-(1-MCH)P:AcCl ratio is 1:2 mol, the yield of 2-hydroxy-5(1-methylcyclohexyl)acetophenone for *para*-(1-methylcyclohexyl)phenol is 61.7%, and the selectivity for the target product is 90.3%.

Acylation reactions of *para*-(1-methylcyclopentyl)-, *para*-(3-methylcyclohexyl), *para*-[3(4)-methylcyclohexen-3-yl-isopropyl]-,

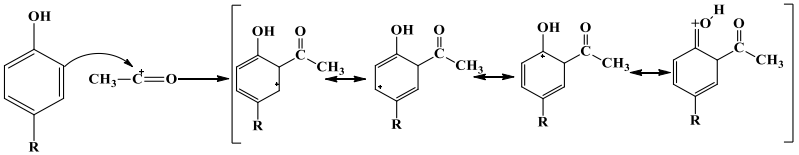
para-arylalkylphenols with acetyl chloride were studied in the presence of $ZnCl_2$ catalyst and it was determined that the yield of cycloalkylacetophenones under the optimal conditions was 46.0-62.5% according to the taken *para*-cycloalkylphenol, and the selectivity of the process was 78.7%-90.3% for the target product.

According to literature sources, the probable mechanism is given for acylation reactions of *para*-alkylphenols with acetyl chloride in the presence of $ZnCl_2$ catalyst.

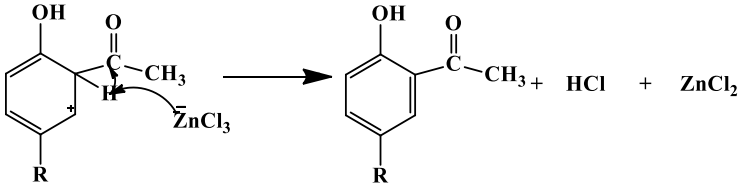
In the first step, acetyl chloride reacts with $ZnCl_2$ to form an acylium ion.



In the second stage, the acylium ion forms a new complex with electrophilic effect of benzene ring. As is evident from the next stage, the acylium ion is resonance stabilized because any new product is formed in this stage. Although a decrease in activity of the product is affected by sensitive electrophiles, it does not affect further reactions.



In the third stage, the proton leaves the complex to return to the benzene ring.



In this stage, $[ZnCl_3]^-$ increases the aromaticity of the ring by removing the proton from the benzene ring, and the final product of

the reaction - acetophenone is obtained.

Acylation reactions of *para*-cycloalkylphenols with acetyl chloride in the presence of γ-Al_2O_3 catalyst impregnated with dispersed $ZnCl_2$

$ZnCl_2$-impregnated γ-Al_2O_3 catalyst of *para*-(1-methylcyclopentyl)-, *para*-[1(3)-methylcyclohexyl], *para*-[3(4)-methylcyclohexen-3-yl-isopropyl]-, *para*-arylalkylphenols acylation reactions were studied in the presence of 20% $ZnCl_2$/γ-Al_2O_3 catalyst at 1:0.5÷3 mol ratios of cycloalkylphenol to acetyl chloride at 120-160°C in 20-60 min.

For example, the results of the acylation reactions of *p*-(1-methylcyclohexyl)phenol with acetyl chloride in the presence of dispersed $ZnCl_2$-impregnated γ-Al_2O_3 catalyst are given in Fig. 2.

The curve in Fig. 2 (a) allows conclude that an increase in the temperature of the acylation reaction from 120 to 140ºC provides an increase in the yield of the target product from 49.3 to 77.4% according to the taken *para*-(1-methylcyclohexyl)phenol, and the selectivity of the process was 93.3-91.7 %. Increase in the reaction temperature to 150-160ºC causes a decrease in the yield of the target product to 66.1%, and the selectivity - from 86.5 to 76.8%. It's explained by the increase in the kinetic energies of the primary components involved in the process at reaction temperature above 140ºC and, as a result, the formation of other isomers in the reaction products. For the purpose of achieving the effective yield of the target product, the effect of the contact time of the primary components with the catalyst was also studied. Fig. 2 (b) represents that conduction of acylation reaction within 20-45 min causes an increase in the yield of the target product from 37.3 to 77.4%, and a decrease in the selectivity from 92.8 to 91.7%. If the meeting period of primary raw materials is increased to 60 min, the yield of the target product increases slightly - 1-2%. Increasing the process time isn't considered efficient due to the small increase in the yield of the target product. Therefore, duration of the catalytic acylation reaction of *para-(*1-methylcyclohexyl)phenol with acetyl chloride is assumed to be continued for 45 min.

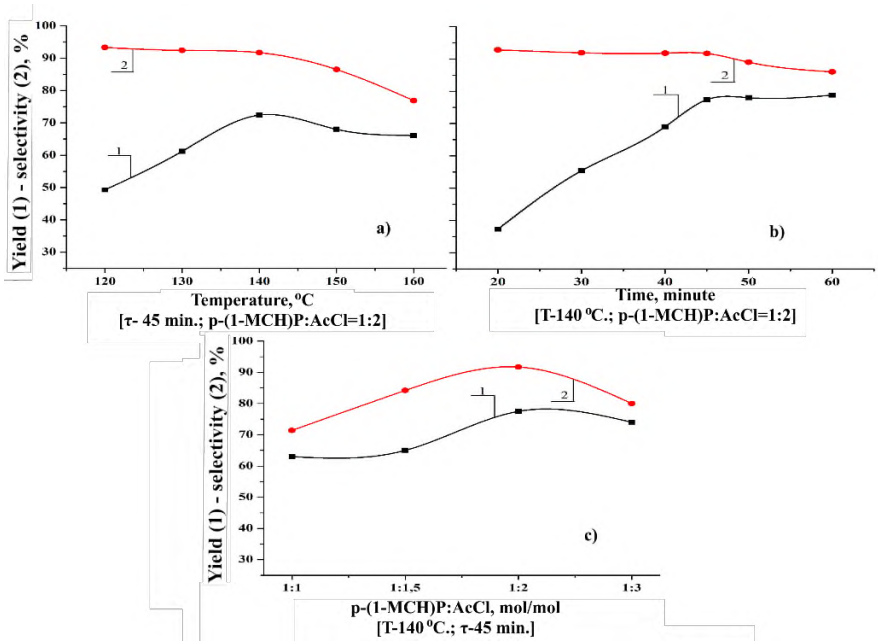


Fig. 2. The results of acylation reactions of para-(1-methylcyclohexyl)phenol with acetyl chloride in the presence of $ZnCl_2$ impregnated γ-Al_2O_3 catalyst

As is seen from Fig. 2 (c), when the mol ratio of *para*-(1-methylcyclohexyl)phenol to acetyl chloride is 1:2, the yield of the target product is 77.4%, and the selectivity is 77.4% for the target product – 2-hydroxy-5(1-methylcyclohexyl)acetophenone is 91.7%. The yield of the target product is not so high at other concentrations of primary raw materials in the reaction mixture.

Effective conditions were found for carrying out acylation reactions of *para*-(1-methylcyclohexyl)phenol in the presence of dispersed $ZnCl_2$ impregnated γ-Al_2O_3 catalyst. It was determined that at the obtained values of the kinetic parameters - temperature - 145ºC, reaction time - 45 min, when the molar ratio of *p*-(1-MCH)P:AcCl is 1:2, the yield of the target product - 2-hydroxy-5(1-methylcyclohexyl)acetophenone is 77.4% according to *p*-(1-MCH)P and the selectivity is 91.7% according to the target product – 2-hydroxy-5(1-methylcyclohexyl)acetophenone.

Similarly, *para*-(1-methylcyclopentyl)-, *para*-(3-methylcyclohexyl)-, *para*-[3(4)-methylcyclohexen-3-yl-isopropyl]-, *para*-arylalkylphenols acetyl chloro acylation reactions were studied in the presence of $ZnCl_2$-impregnated γ-Al_2O_3 catalyst. At this time, the yield of the target products was 61.7-77.4% according to the *para*-cycloalkylphenol and the process selectivity was 87.5-91.9% according to the target product.

Study of acylation reactions of *para*-cycloalkylphenols with acetyl chloride in presence of KU-23 catalyst

Acylation reactions of *para*-(1-methylcyclopentyl)-, *para*-*[*1(3)-methylcyclohexyl], *para*-[3(4)-methylcyclohexen-3-yl-isopropyl]-, *para*-arylalkylphenols were studied in the presence of KU-23 catalyst at 120-160°C during 4-8 h, in 1:0.5÷3 mol ratios of phenol to acetyl chloride, and the amount of catalyst was 10-15%.

For example, the results of the acylation reactions of *p*-(1-methylcyclohexyl)phenol in the presence of KU-23 catalyst with acetyl chloride are given below.

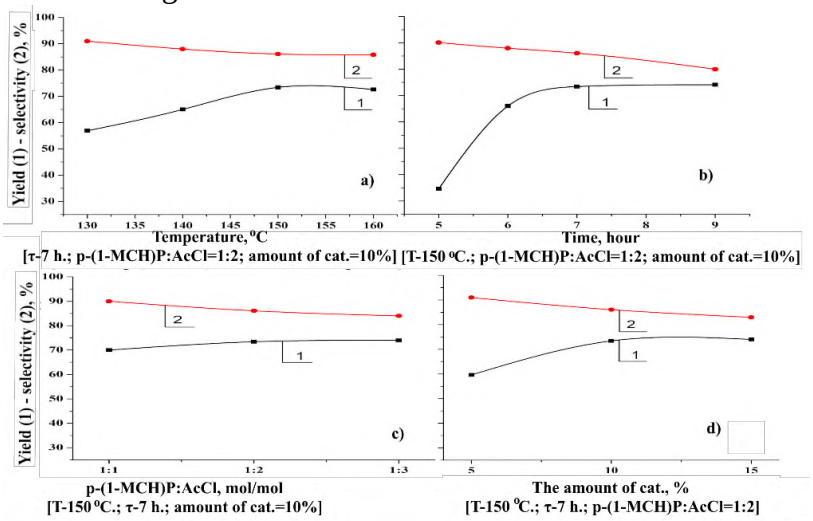


Fig. 3. The results of acylation reactions of para-(1-methylcyclohexyl)phenol with acetyl chloride in the presence of KU-23 catalyst

It can be seen from Fig. 3 that when the temperature of the acylation reaction is increased from 130 to 150°C, the yield of the target product increases from 56.9 to 73.4%. In the subsequent increase of the reaction temperature, the yield of the target product decreases to 72.6%, the selectivity of the process decreases from 86.1 to 85.8%. An increase in the reaction time from 5 to 7 h causes an increase in the yield of the target product from 34.6 to 73.4%. Under these conditions, the selectivity of the process is within 86.1-90.1%. When the reaction time is increased to 8-9 h, the yield of the target product remains unchanged (74.1%), but a decrease is observed in selectivity of the process. The curve (c) in Fig. 3 represents a 1:2 mol. ratio of *para*-(1-methylcyclohexyl)phenol to acetyl chloride is more suitable, because under these conditions the yield of the target product is 73.4% according to the alkylphenol), and the selectivity is 86.1% for the target product. Increasing the amount of acetyl chloride in the reaction mixture does not affect the yield and selectivity of the target product; both indicators remain at approximately the same level. Fig. 3 allows observe that the yield of the target product is 59.8% by using 5% KU-23 catalyst for the acylation reaction (according to alkylphenol). 97-98% of high selectivity is achieved since the reaction is not complete. Effective yield (73.4%) and selectivity (86.1%) of the target product are obtained when the amount of catalyst is 10%.

As a result of studying the effect of various kinetic parameters on the yield and selectivity of the target product, the following conditions can be considered optimal for the acylation reaction of *para*-(1-methylcyclohexyl)phenol with acetyl chloride using the KU-23 catalyst: temperature−150°C, reaction time - 7 h. The molar ratio of *para*-(1-methylcyclohexyl)phenol to acetyl chloride is 1:2, the consumption of the catalyst is 10% (according to the *para*-(1-methylcyclohexyl)phenol). The yield of the target product is 73.4%, and the selectivity for the target product is 86.1% under these conditions.

Similarly, acylation reaction of *para*-(1-methylcyclopentyl)-, *para*-(3-methylcyclohexyl), *para*-[3(4)-methylcyclohexen-3-yl-isopropyl]-, *para*-arylalkylphenols with acetyl chloride in the presence of KU-23 catalyst were studied and it was determined that the yield of cycloalkylacetophenones in optimal conditions is 57.7-79.4%, and the

selectivity is 84.5-90.7%.

Study of acylation reactions of *para*-cycloalkylphenols with benzoyl chloride in the presence of dispersed $ZnCl_2$-impregnated γ-Al_2O_3 catalyst

$ZnCl_2$-impregnated γ-A_2O_3 catalyst of *para*-(1-methylcyclopentyl)-, *para*-[1(3)-methylcyclohexyl], *para*[3(4)-methylcyclohexen-3-yl-isopropyl]-, *para*-arylalkylphenols acylation reactions with benzoyl chloride were studied in the presence of 20% $ZnCl_2$/γ-Al_2O_3 catalyst at 120-160°C, during 20-60 min, in 1:1÷3 mol ratios of cycloalkylphenol to benzoyl chloride.

For example, the results of acylation reactions of *p*-(1-methylcyclohexyl)phenol with benzoyl chloride in the presence of dispersed $ZnCl_2$-impregnated γ-Al_2O_3 catalyst are given in Fig. 4.

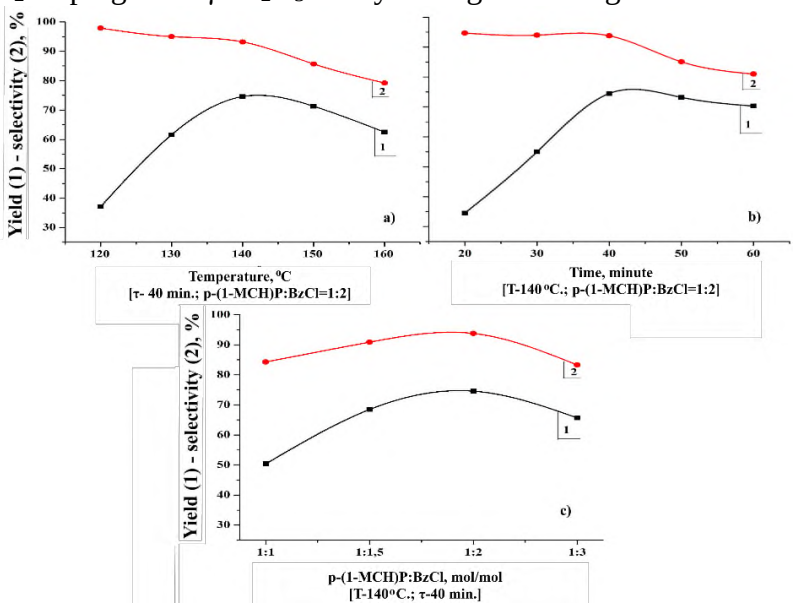


Fig. 4. The results of acylation reactions of para-(1-methylcyclohexyl)phenol with benzoyl chloride in the presence of dispersion $ZnCl_2$ impregnated γ-Al_2O_3 catalyst

The curve (a) in Fig. 4 allows conclude that an increase in the temperature of the acylation reaction from 120 to 140ºC causes an increase in the yield of the target product from 34.5 to 74.6% of *para*-

(1-methylcyclohexyl)phenol. An increase in the reaction temperature up to 150-160ºC leads to 66.1% of decrease in the yield of the target product. It's explained by the increase in the kinetic energies of the primary components involved in the process at the reaction temperature above 140ºC and, results in the formation of other isomers in the reaction products. Effect of the contact time of the primary components with the catalyst is also important in order to achieve the effective yield of the target product. Fig. 4(b) shows that the yield of the target product increased from 34.5 to 74.6% when the acylation reaction was carried out in 20-45 min. When the meeting period of primary raw materials is increased to 60 min, the yield of the target product changes slightly - 1.4%. Due to the slight increase in the yield of the target product, taking longer the reaction time cannot be considered efficient. Therefore, the time of the acylation reaction of *para*-(1-methylcyclohexyl)phenol with benzoyl chloride is 40 min. As is evident from Fig. 4, when the molar ratio of *para*-(1-methylcyclohexyl)phenol to benzoyl chloride is 1:2, the yield of the target product is 74.6%.

Effective conditions were found for carrying out acylation reactions of *para*-(1-methylcyclohexyl)phenol with dispersed $ZnCl_2$ impregnated γ-Al_2O_3 catalyst with benzoyl chloride. It was determined that at the obtained values of the kinetic factors: temperature – 140ºC, reaction time – 40 min, *p*-(1-MCH)P:BzCl to mol. ratio 1:2, the yield of the target product - 2-hydroxy-5(1-methylcyclohexyl)benzophenone according to *p*-(1-MCH)P is 74.6%, and the selectivity of the process is 93.8% according to the target product.

Study of acylation reactions of para-cycloalkylphenols with acetic acid in the presence of dispersed $ZnCl_2$-impregnated γ-Al_2O_3 catalyst

$ZnCl_2$-impregnated γ-Al_2O_3 catalyst of *para*-(1-methylcyclopentyl)-, *para*-[1(3)-methylcyclohexyl], *para*[3(4)-methylcyclohexen-3-yl-isopropyl]-, *para*-arylalkylphenols acylation reactions with acetic acid were studied in the presence of 20% $ZnCl_2/\gamma$-Al_2O_3 catalyst at 1:1÷3 mol. ratios of cycloalkylphenol to benzoyl chloride at of 120-160°C in 20-60 min.

For example, the results of the acylation reactions of *p*-(1-methylcyclohexyl)phenol with dispersed $ZnCl_2$-impregnated γ-Al_2O_3 catalyst with acetic acid are given in Fig. 5.

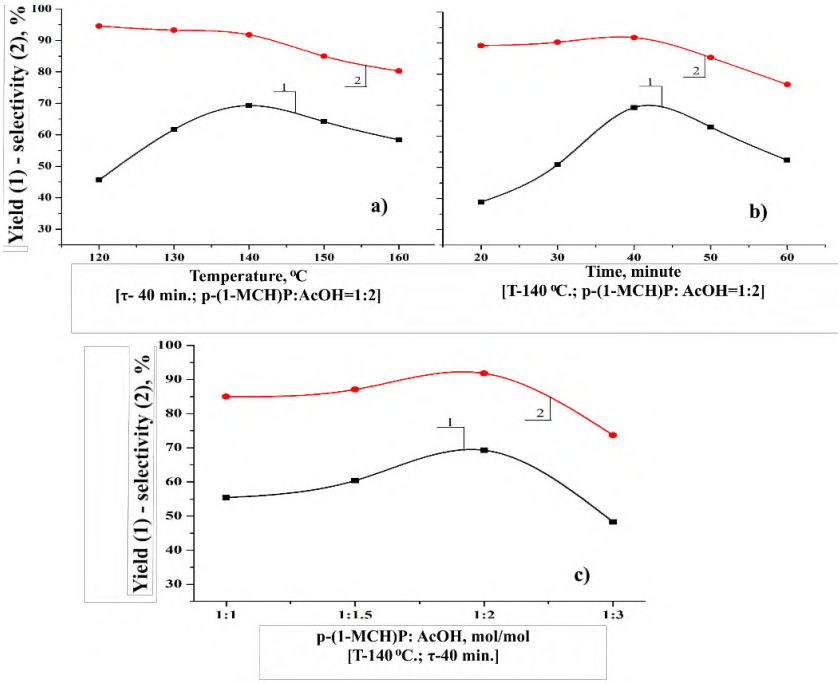


Fig. 5 The results of acylation reactions of para-(1-methylcyclohexyl)phenol with acetic acid in the presence of $ZnCl_2$ impregnated γ-Al_2O_3 catalyst

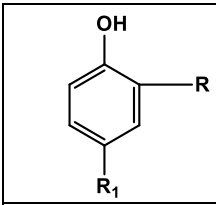
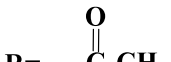
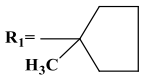
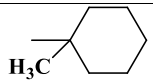
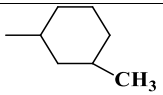
The curve (a) in Fig.5 allows conclude that by increasing the temperature of the acylation reaction from 120 to 140ºC, the yield of the target product increased from 45.5 to 69.3% for *para*-(1-methylcyclohexyl)phenol. An increase in the reaction temperature to 150-160ºC causes a decrease in the yield of the target product to 64.2-58.4%. It's explained by the formation of other isomers in the reaction products as a result of the initial components involved in the process at the reaction temperature above 140ºC. As is evident from Fig. 4 (b), when the acylation reaction was carried out in 20-40 min, the yield of the target product increased from 38.8 to 69.3%. When the meeting period of primary components was 60 min, the yield of the target product was decreased to 52.3%. It's seen from Fig. 4, that mol. ratio of

para-(1-methyl-cyclohexyl)phenol to acetic acid is 1:2, the yield of the target product - 69.3%, and the selectivity - 91.8%. At other concentrations of primary raw materials in the reaction mixture, the yield of the target product is not so high. Effective conditions were found for carrying out acylation reactions of *para*-(1-methylcyclohexyl)phenol with dispersed $ZnCl_2$-impregnated γ-Al_2O_3 catalyst with acetic acid: temperature - 140ºC, reaction time - 40 min., the mol. ratio *p*-(1-MCH)P to AcOH is 1:2, the yield of the target product - 2-hydroxy-5(1-methylcyclohexyl)acetophenone is 69.3% according to *p*-(1-MCH)P, and the process selectivity is 91.8% according to the target product. .

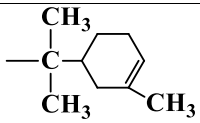
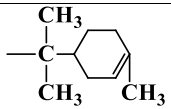
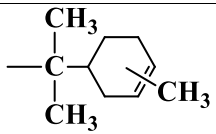
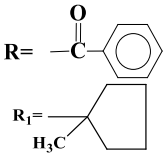
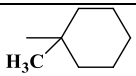
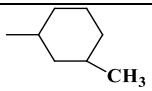
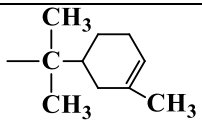
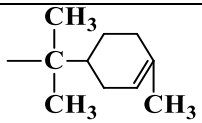
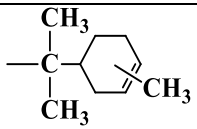
Physico-chemical properties and elemental compositions of the synthesized cycloalkylaceto- and benzophenones are set into tab. 1.

Table 1.

Physico-chemical properties and elemental compositions of the synthesized cycloalkylaceto- and benzophenones

	$T_{boil.}$ **10 mm Hg, °C**	**Melting temp., °C**	**Mol. mass**	**Calculated, % Found, %**	
				C	**H**
1	2	3	4	5	6
Where  	150 –152	113.3	218	77.1 / 76.6	8.2 / 7.8
	166 – 168	114.8	232	77.5 / 76.9	8.6 / 8.2
	161– 163	123	232	77.5 / 76.7	8.6 / 8.0

Cont. of Tab.1

1	2	3	4	5	6
	203 – 205	106-107	272	79.4 78.9	8.8 8.5
	208 – 212	108 - 110	272	79.4 79.7	8.8 9.3
	202 – 212		272	79.4 78.7	8.8 8.5
–arilalkil	192 – 200		241	80.0 79.1	6.7 5.9
Where 	160-162	95	280	81.4 80.6	7.1 6.7
	176-177	104	294	81.6 80.8	7.5 7.1
	172-174	76	294	81.6 81.0	7.5 6.8
	191-194	123	334	82.6 81.7	7.8 7.3
	201-203	126	334	82.6 81.5	7.8 6.8
	196-198	-	334	82.6 81.3	7.8 7.1
–arilalkil	188-191	-	302	83.4 82.6	6.0 5.3

Study of Application Fields of

2-Hydroxy-5-Methylcycloalkylaceto- and benzophenones

2-Hydroxy-5-methylcycloalkylaceto- and benzophenones were tested as an antioxidant for diesel fuel, a stabilizer and antirad against radiation for polyethylene.

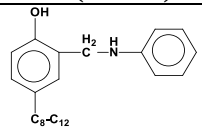
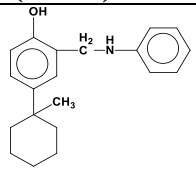
Tests of 2-hydroxy-5-methylcycloalkylacetophenones as an antioxidants in diesel fuel

The samples were prepared by adding 0.004% of known and proposed antioxidants to diesel fuel. The samples were tested in LSART apparatus in diesel fuel according to GOST 305-82 as an antioxidant. The amount of sediment formed in the fuel was determined after heating the primary diesel fuel and antioxidants-added samples for 4 h at 120°C in a closed crucible.

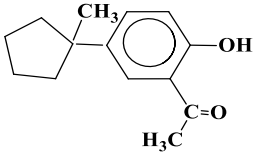
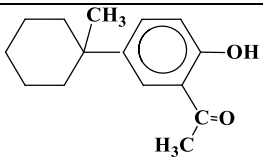
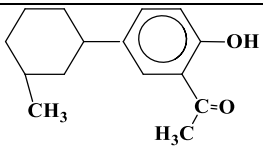
The results of comparative tests of proposed and known antioxidants on diesel fuel are given in Tab. 2.

Table 2.

Test results of the 2-hydroxy-5-methylcycloalkylacetophenones as an antioxidants for diesel fuel

№	ANTİOXIDANTS	AO amount, %	Sediment amount, mg/ 100 cm^3
1	2	3	4
1.	DF (without addition of AO)	-	4.35
2.	DF+ionol (known)	0.004	1.0
3.	 DY + (known)	0.004	0.9
4.	 DY + (known)	0.004	0.7

Cont. of Tab.2

1	2	3	4
5.	 DY +	0.004	0.18
6.	 DY +	0.004	0
7.	 DY +	0.004	0.1

It can be seen from the table that when the proposed samples were added to diesel fuel, compared to known antioxidants, after oxidation at 120°C for 4 hours, the amount of sediment in diesel fuel was 0.1-0.18 mg/100 cm^3, and in sample (6) no sediment was formed.

Tab. 3 shows the specified flash point of diesel fuel after adding 2-hydroxy-5-methylcycloalkylacetophenones.

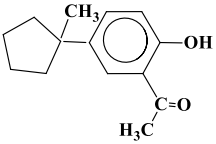
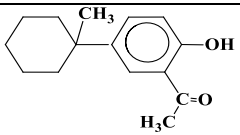
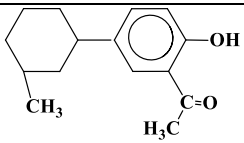
It's evident from Table 3 that after adding 0.004% of 2-hydroxy-5-methylcycloalkylacetophenones to diesel fuel, flash points of diesel fuel were 57.3-58.7°C respectively, meeting the requirements of the EN-590 standard for diesel fuels.

Table 3.

Flash point of diesel fuel after addition of 2-hydroxy-5-methylcycloalkylacetophenones

No.	Nomenclature	Flash point in closed crucible , °C
1.	**2.**	**3.**
1.	According to EN-590	Minimum 55

Cont. of Tab.3

1	2	3
2.	 DY +	57.3
3.	 DY +	58.7
4.	 DY +	58.0

2-Hydroxy-5-methylcycloalkylacetophenones are dielectric, when added to hydrotreated diesel fuel, the flash point of diesel fuel is in the range of 57.3-58.7°C in accordance with the requirements of EN-590 standard, it prevents the risk of fire under external influences during the storage of fuel in tanks and transportation.

Specific electrical conductivity of hydrotreated diesel and diesel fuel with 0.004% cycloalkylacetophenone added was determined in EL-4M apparatus in accordance with GOST-25950. It was determined that after adding 0.004% of 2-hydroxy-5-methylcycloalkylacetophenones to diesel fuel, the electrical conductivity of diesel fuel remains stable. It proves that the antioxidant does not have a negative effect on the electrical conductivity of diesel fuel

Tests of 2-hydroxy-5-methylcycloalkylaceto- and benzophenones as stabilizers in high density polyethylene

Tests of 2-hydroxy-5-methylcycloalkylaceto- and benzophenones as stabilizers in high-density polyethylene were carried out at "Physico-Mechanical Researches of Polymer Materials" department of Sumgayit Polymer Materials Institute of the Ministry of Science and Education of the Republic of Azerbaijan. Strength limits and relative elongations of samples obtained on the basis of polyethylene and cycloalkylaceto-, benzophenones (1-3%) were determined. The tensile

strength of the received composition samples was 6.2-6.8 kg (at a pressure of 9.35-10.92 MPa), the relative elongation was 141.2-181.2 mm (585-725%), so that which is superior to the НГ-2246 stabilizer used in industry for this purpose.These properties suggest that the proposed cycloalkylaceto- and benzophenones are completely soluble in these compositions, the intermolecular connections are strong, and these properties are determined by its relative elongation .Thus, the results of tests of the obtained products as stabilizers in high-pressure polyethylene are satisfactory and may be recommended for this purpose.

Tests of 2-hydroxy-5-methylcycloalkylbenzophenones as antirads in high-density polyethylene

The tests of 2-hydroxy-5-methylcycloalkylbenzophenones as antirad against radiation in high-density polyethylene were carried out in the "Radiation Physics of Polymer and Electroactive Materials" laboratory of the Institute of Radiation Problems of the Ministry of Science and Education of the Republic of Azerbaijan.

The samples were prepared by adding 3-10% 2-hydroxy-5(1-methylcyclopentyl)benzophenone to high-density polyethylene granules by mechanical stirring and thermal pressing. At this time, the composition was pressed at 120°C in 5 min; it was followed by cooling at room temperature and removed from the molds. The obtained layer was cut in a standard shape. Temperature dependences of dielectric permittivity - ε and specific resistance - ρ 293-433K using two contact methods before and after γ-irradiation in the interval of 50-200 kQr in the MRX-γ-25M device operating on the basis of Co^{60} isotope were studied and analyzed comparatively. As a result of the measurement of dielectric parameters, it was determined that the polarity of the polymer with cycloalkylbenzophenone added was higher and this additive may be used for increasing the polarity of polymers.

CONCLUSIONS

1. Acylation reactions of *para*-[1(3)-methylcyclohexyl]phenols, *para*-(1-methylcyclopentyl)phenol, *para*-[3(4)methylcyclohex-en-3-yl-isopropyl]phenols with acetyl chloride were studied in the presence of $ZnCl_2$-impregnated γ- Al_2O_3 catalyst. It was determined that the yield of cycloalkylacetophenones according to *p*-CAP was 61.7-77.4% and the process selectivity according to the target product was 87.5-91.9% in the found optimal conditions – temperature - 140-150°C, time - 40-50 min, molar ratio of *p*-cycloalkylphenol to acetyl chloride - 1:2.
2. Acylation reactions of *p*-CAP with acetyl chloride were studied in the presence of $ZnCl_2$ and KU-23 catalysts and it was determined that the yield of cycloalkylcetophenones was 46.0-62.5% in the presence of $ZnCl_2$ catalyst and the process selectivity was 78.7%-90.3% for the target product and the yield of target products was 57.7-79.4%, selectivity - 84.5-90.7% using the KU-23 catalyst [7, 8, 15, 22, 23, 24, 25].
3. Acylation reactions of *para*-[1(3)-methylcyclohexyl]phenols, *para*-(1-methylcyclopentyl)phenol, *para*-[3(4)methylcyclohex-en-3-yl-isopropyl]phenols with benzoyl chloride were studied in the presence of γ-Al_2O_3 catalyst impregnated with dispersed $ZnCl_2$. The yield of cycloalkylbenzophenones was 62.6-74.6% for the *para*-cycloalkylphenol and the process selectivity was 85.8-93.8% according to the target product under the optimal conditions (temperature-140-160°C, time - 40-55 min, mol. ratio of *p*-cycloalkylphenol to benzoyl chloride-1:2) [1, 16, 18, 21].
4. Acylation reactions of *para*-cycloalkylphenols with acetic acid were studied in the presence of γ-Al_2O_3 catalyst impregnated with dispersed $ZnCl_2$. The yield of the target products according to *para*-cycloalkylphenol was 57.7-69.3%, at 135-160°C, in 30-50

min in a 1:2 mol ratio of *para*-cycloalkylphenol to acetic acid, and the process selectivity according to the target product was 84.8-91.8% [2, 4, 5, 9, 10, 12, 13, 14, 17, 19].

5. Synthesized 2-hydroxy-5-methylcycloalkylacetophenones were tested as antioxidants for diesel fuel. 2-hydroxy-5-methylcycloalkylacetophenones were added to diesel fuel at 0.004%, no precipitate is formed after oxidation at 120°C during 4 h [20].
6. 2-Hydroxy-5-methylcycloalkylaceto- and benzophenones were tested as stabilizers to high-pressure polyethylene in the amount of 1-3% and it was determined that the tensile strength of polyethylene was 6.2-6.8 kg (9.35-10.92 MPa in pressure), relative elongation was 141.2-181.2 mm (585-725%) [3, 6].
7. Dielectric permeability of 2-hydroxy-5(1-methylcyclopentyl)-benzophenone (3-10%) and high-density polyethylene layers before and after γ-irradiation in the range of 50-200 kQr in the MRX-γ-25M device operating on the basis of the Co^{60} isotope and the temperature dependences of specific resistance 293-433K were studied and it was determined that polarity of cycloalkylbenzophenone-added polymer was higher and the added additives may be used to increase the polarity of polymers [24].

MAIN CONTENT OF THE DISSERTATION PUBLISHED IN WORKS:

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