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ABSTRACTS

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Scientific Program of the Conference

- Plenary Lectures (25 and 40 min)
- Oral Reports (up to 20 min)
- Poster Session and Round Table

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Abstracts published in author's edition.

Plenary Lectures

CURRENT TRENDS IN CHEMISTRY AND TECHNOLOGY OF RARE AND DISPERSED ELEMENTS OF III–VIII GROUPS OF THE PERIODIC TABLE

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The present report summarizes some promising directions in the chemistry and technology of rare and dispersed elements, made by the employees (heads of the directions are mentioned in the text) of the Department of Chemistry and Technology of Rare and Dispersed elements named after K.A. Bolshakov, recently.

Progress in the technology of rare and dispersed elements (RE – no canonical definition, their number varies from 40 to 44 depending on the classification) and functional materials based on them necessarily supposes involvement in the area of practical use of modern achievements in fundamental research in chemistry and metallurgy of these metals. Technological aspect of the problem combines objectives of extraction, separation and purification of the RE compounds in the processing of primary and technogenic raw materials with the task of oriented search and creation reproducible technologies to produce a new generation of functional materials based on them with the necessary complex of consumer properties and qualities.

Work is devoted to the presentation of the results: creation of high effective extraction processes of associated retrieve of gallium and vanadium during processing of aluminum raw materials; the use of methods of "molecular design" for choosing an extractant for associated scandium extraction of products of spongy titanium production; the use of the method of "molecular detection" in the refining of platinum group metals; description of application of "soft" chemistry (in the framework of alkoxy technology) for production of functional materials based on refractory metals of d-elements of V–VIII groups; the use of supercritical CO_2 for the synthesis of ultrafine (nano scale) materials based on the RE.

The research was carried out under the support of RFBR, grants No. 09-03-00328a and 12-03-00699a.

OXIDATIVE CHLORINATION OF HYDROCARBONS

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Oxidative chlorination (or oxychlorination) is the process of the hydrocarbons chlorination carried out in the presence of oxidizing agents. As usual these agents are oxygen or air. The source of chlorine is the gaseous hydrogen chloride. The necessity of great quantities hydrogen chloride utilization is the main reason of elaboration of the oxychlorination method.

As usual the process is realized over the redox catalysts in particular $CuCl_2$/support – known as the Deacon catalyst.

The process based on the reaction of hydrogen chloride oxidation by the oxygen (air):

$2HCl + 0,5O_2 \Leftrightarrow Cl_2 + H_2O$

The Deacon reaction is reversible, proceeding at the temperature interval 350–450°C. The rise of temperature leads to decrease of chlorine balance yield and accordingly to decrease of hydrogen chloride and oxygen conversion.

In dependence from the nature of the initial hydrocarbon and conditions the oxychlorination processes can proceed by the different mechanisms. Only paraffins oxychlorination processes (substitutive oxychlorination) include the preliminary chlorine formation by the Deacon reaction.

The combination of the Deacon and chlorination reactions leads to the change of equilibrium and practically complete of hydrogen chloride conversion. The oxychlorination reactions are practically irreversible at the process temperatures.

The most effective catalysts of these processes are mixture of cupric chloride with chlorides of alkali and rare earth metals. Such catalytic systems have a low volatility of Cu salts and more high activity. The activity increase is the function of the oxygen adsorption rate. The catalyst with molar ratio $KCl/CuCl_2 = 0,5$ has a maximum activity on the value of the constant rate.

The research data of Deacon reaction has appeared the important base for study of the paraffins, first of all methane and ethane, oxychlorination processes,. It was connected with high practical importance of the number chloroorganic compounds such as chloroform, methyl chloride, vinyl chloride.

It was shown for the **methane oxychlorination process** that the combination of the reactions of hydrogen chloride oxidation and substitutive oxychlorination does not influence on the rate of Deacon reaction. Besides that these reactions proceed on the different active centers. The rates of the reactions of methane and its chloroderivative compounds oxidation are submitted by the equations of the first order on the oxygen and organic substrate.

The technology of the methane oxychlorination process was elaborated by us at the end of XX century. The combination of the chlorination and oxychlorination stages allows to create the balanced on the chlorine process of the chloromethanes obtaining. The process is characterized by the practically complete of chlorine use combined with minimum wastes.

The methane oxychlorination process can have the certain manufacturing perspectives. It is connected with elaboration by us the technology of the methyl chloride pyrolysis to the light olefins. Hydrogen chloride emitted under pyrolysis is returned to the methane oxychlorination process with primary methyl chloride obtaining.

The ethane oxychlorination process is characterized side by side with Deacon and chlorination reactions by the proceeding of the reactions of the aliphatic hydrocarbons dehydrochlorination with chloroolefins obtaining. The activation energy of paraffins (130 kJ/mol) and olefins (40–90 kJ/mol) transformation is different. Because of that the increase of temperature leads to the rise of the alkenes yield. The carbon oxides are formed in the main from ethylene and chloroethylenes. Herewith the introduction of one chlorine atom to the ethylene increase the rate constant of deep oxidation in 7-8 times.

The researches of the ethane oxychlorination process technology show that over the $CuCl_2$-KCl/support catalysts at 500–550°C the summary yield of vinyl chloride and ethylene reaches up to 80%. The summary heat effect is equal by 300 kJ/mol; it is necessary to take into account at the elaboration of the technological scheme.

By analogy the oxychlorination of 1,2-dichloroethane proceeds over the Cu-containing catalyst at 350–400°C. The main products are trichloroethylene and perchloroethylene.

The additive oxychlorination of ethylene is related to the group of reactions which do not require the preliminary oxidation of hydrogen chloride to chlorine. As usual the process proceeds over the $CuCl_2/Al_2O_3$ catalyst at 210–260°C. The oxychlorination mechanism includes the stage of ethylene chlorination by cupric chloride with following re-oxidation of cuprous chloride.

The nature of support plays an essential role at the process proceeding. Alumina does not an inert support but it interacts with the salt phase components. The use of gamma-alumina leads to the rise of the acceptor ability of the Cu-cation by means of formation of bridge bonds between Cu and support cations. This facilitates the rupture of ethylene double bond at its interaction with Cu cations. Hydrogen chloride takes part in the increase of the salt phase dispersion on the catalyst surface. The role of oxygen is is the oxidation of Cu^+ to Cu^{2+} and promotion of the migration of Cl-ions with $CuCl_2$ formation. The rate of the ethylene oxychlorination reaction is limited or by stage Cu reduction by ethylene or by stage of Cu re-oxidizing. The activation energy of the reaction is 60–80 kJ/mol.

Now the ethylene oxychlorination process with 1,2-dichloroethane formation in the vinyl chloride manufacture structure is the only realized oxychlorination process in industry. The indexes of the ethylene oxychlorination processes depend on methods of their realization. In the whole the all industrial processes can be classify on the two main signs: (1) the systems with fluidized or fixed bed catalyst and (2) the systems with use of air or concentrated oxygen.

The process in the fluidized bed catalyst is the most spread in the industrial practice in the world and in particular, in Russia. It is showed by us that the best exploiting properties are characterized for fluidized bed catalysts having the minimum Cu quantity on the external catalyst surface. This structure of the catalyst allows to carry out the ethylene oxychlorination process at the minimum exceed of ethylene and oxygen on the relation to hydrogen chloride.

The most principal problem at the catalyst choice is the selectivity of dichloroethane formation. In the structure of by-products formation approximately 70% of ethylene is transformed to the carbon oxides; the rest of ethylene is transformed to the secondary chloroorganic compounds – 1,1,2-trichloroethane, chloroform and others.

The deep oxidation products (CO_x) are formed both from ethylene and 1,2-dichloroethane. The ratio of rate constants of dichloroethane and ethylene deep oxidation is 2:1 in the conditions of the oxychlorination process. The rise of temperature promotes by increase of the part of dichloroethane oxidation. The activation energy of the oxidation reaction is more than the same parameter for oxychlorination reaction upon 17-30 kJ/mol. It explains the fact of decrease of dichloroethane formation selectivity at the rise of temperature. The hydrogen chloride brakes the reactions of deep oxidation in the conditions of oxychlorination process.

The use of the catalysts with minimum content of Cu at the external surface of grain ensures the yield of carbon oxides no more than 1,5% on the ethylene fed.

The reserve of the ethylene oxychlorination progress is the use the catalysts with falling activity. This can be reached by introduction of the chlorides of alkali- or alkali-earth metals to the catalyst. The low activity may be compensated by temperature increase and contact time decrease. At these conditions the productivity can be increase in two times.

SUPERCRITICAL FLUID TECHNOLOGY IN CHEMISTRY

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The supercritical fluid (SCF) – a substance at a temperature and pressure above the critical point, determined by temperature and pressure T_{crit} and P_{crit} in which no distinction between liquid and gas. A large number of substances can be in the supercritical state, actually, move into a supercritical state is limited by the decomposition temperature of the substance. The most easily obtainable supercritical state for such compounds as CO_2, H_2O, NH_3, N_2O, CH_4, C_2H_6, C_3H_8. Number of physical properties of supercritical fluids are something intermediate between a liquid and a gas. Carbon dioxide, nitrous oxide, ethylene and some other gases in a SCF acquire the ability to dissolve many organic substances. Now 90% of SCF technologies focused on supercritical CO_2.

Processes in the environment of supercritical fluids are realized in nature. For example, the formation of natural minerals, in particular quartz crystals derived from the supercritical fluid and is reproduced in the technology of piezo-quartz. There are an indication that near the boundary of the magma in supercritical fluid processes of formation of saturated hydrocarbons are going.

Supercritical fluids have been used in processes such as supercritical fluid extraction, chromatography, supercritical drying, impregnation, particle micronization. SCF technology can solve the problem of making microparticles with a narrow size distribution of substances not stable when heated. Micronization is one of the most popular and emerging trends in the industries such as pharmaceutical, food, cosmetics, explosives, and many others.

RESS technology (Rapid Extension of a Supercritical Solution) used for substances soluble in SC-CO_2 – the solution is sprayed through a nozzle into a collection of atmospheric pressure, the carbon dioxide evaporates almost instantaneously and the powder is deposited in the collection. This scheme allows you to control the conditions of powders and influence the size and morphology of the particles.

If substances are poorly soluble in SC CO_2, SAS (Supercritical Anti-Solvent) technology is used – an aqueous or organic solution of the substance is injected into the high-pressure chamber with supercritical CO_2. When the precipitation is not soluble in the SC CO_2 particulate matter to the bottom of the vessel and CO_2 together with the substances dissolved therein removed.

Process PGSS (Particles from Gas Saturated Solutions) is also interesting – in this case, the viscous substance saturated SC CO_2, achieving the desired consistency, and then the substance is forced out of the nozzle. An instantaneous expansion of the gas, which provides excellent process parameters.

Method for the synthesis of nano-dispersed simple and complex oxides by precipitation with supercritical CO_2 antisolvent (SAS) is promising. This method satisfies requirements of obtaining high/chemically pure product with a narrow particle size distribution, a high porosity and a large surface area values and can be implemented in production, taking into account the principles of "green chemistry".

DESIGN OF RECYCLING SYSTEM

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At the beginning of the XXI century the policy of the industrialized states departs from "weak" management in a format "addresses with waste" to model on the basis of the concept "zero waste". The philosophy of "cradle to grave" is succeeded by the new one – "cradle to cradle" or the "C2C-cycle", leaning on the concept "Zero Waste", Life Cycle Assessment and Recycling. The linear economy gives way to cycle economy. It switches attention to processes of designing and production of recyclability products. Without this primary factor the waste processing industry is a kind of consigning to the past "the pipe end" approach. Existence of waste processing technologies doesn't solve a problem without creation of suitable network structures which allow to use technological capabilities. In the modern urbanized systems the recycling carries out the infrastructure function which content is beyond the scope of "waste management". However usually intercompany recycling activities are regarded by the company representatives as bilateral market transactions, not as collaborative network activities [1]. The state lacks the public policy that will transform its waste management system into a recycling system.

The known hierarchy of waste management (hierarchy of political preferences/opportunities) or "ladder" of the Dutch politician of Lansink (1979), can be considered as an illustration of wastecentric approach (WCA) at which the 4th level of hierarchy is allocated for a recycling. For recycling society the hierarchy of scientific and technical decisions – cyclecentric approach (CCA) has advantage. These approaches are qualified respectively as 1) Hierarchy of political preferences and 2) Hierarchy of scientific and technical decisions.

Offered CCA is based on three provisions: *1) recycling – a hierarchical network of material streams in which waste is one of states; 2) objects of research, designing and management are processes, technologies and recycling networks; 3) the safe exit of a material stream from anthropogenic in a natural cycle is provided with assimilatory technologies.* The waste management is transformed to management of a recycling networks.

We were the first to publish the known definition of the recycling system, overcoming convention of technical basis isolation, management and environment factors:

$$\boldsymbol{S_{def} \equiv \langle Z, STR, TECH, COND \rangle}$$

where ***Z*** – set of recycling objectives; ***STR*** – set of the structures to carry out the purposes; ***TECH*** – set of technologies (methods, means, algorithms, etc.), implementing recycling; ***COND*** – recycling existance conditions (external and internal), including legal, economic, ecological, social aspects.

The project of a recycling is based on the following provisions of CCA: 1) recycling – a network of material streams in which waste is one of status; 2) the exit of a material stream from technogenic to the environmental cycle has to be provided with assimilatory technologies; 3) objects of designing and management are processes and recycling networks.

The project of potential network structure of a recycling (PPNSR) includes two stages: 1) development of heuristic structure, 2) designing of reverse logistics infrastructure for recycling with GIS-technology for locating sorting facilities, of the storage, processing (recycling plants) facilities across the network. The objective of first stage is to decide the processing (recycling plants) facilities alternatives across the network. And the second stage is to decide the location of the reuse alternatives, collection and storage points alternatives, sorting alternatives, processing alternatives (recycling plants) facilities across the network. By analogy to the best available techniques (BAT) it is possible to identify the best available recycling networks (BARN). The best conditions for designing and adaptation of recycling systems are created and provided in a recycling cluster.

One way of describing closed-loop systems as a model is to display them as nets or graphs. Möller (1994) introduced the «material flow nets» in which the nodes are interpreted as transformation processes and the arrows as material flows. This can be done empirically by measuring, but calculations based on mathematical models are also possible. The available mathematical models include optimization models, such as linear programming (LP), mixed-integer linear programming (MILP), nonlinear programming (NLP), dynamic programming (DP), and multi-objective programming (MOP). The methodology described above is ideally suited for analysing production and waste disposal structures. This increased understanding will help to guide the designing of recycling systems.

Example of design of the return network is paper [2]. Besides, complex decisions are perspective. For example, the SAP AG corporation develops the complex software product "SAP Waste and Recycling" providing planning of resources, the mobile Solutions for the Internet, GIS, optimal logistics, calculations for services and others.

This system approach is based on the analysis and synthesis of foreign publications in: Reverse Logistics Magazine, Omega (The International Journal of Management Science), International Journal of Advanced Manufacturing Technology, Robotics and Computer-Integrated Manufacturing, Construction & Demolition Recycling, Waste Management, Ecological Economics, European Journal of Operational Research, Journal of Environmental Engineering, Journal of Industrial Ecology, Environmental Modelling & Software, and others.

The main scope of researches: Recycling Enterprises, Recycling Plant, Designing With The End In Mind, Life Cycle Analysis and Recycling, Analysis of Recycling Systems, Recycling and Green Chemistry, Reprocessing, Network Design Project, Reverse Logistics, Design for 'R' (Design for Reuse, Remake and Recycling), Design for Disassembly (DFD), Design for Environment (DFE), Design for Reincarnation, Design Total Recycling Systems, Modeling of Recycling, Systems Modeling in the Design of Reverse Logistics Infrastructure for Recycling, Best Environmental Practices for Recycling, Best Available Treatment Recovery and Recycling Techniques (BATRRT), Web-based DSS (The Recycling Decision Support System), Deterministic inventory model for recycling system.

In the report there are considered the evolution of standard network structures of a recycling, their classification and classification of technologies by an adaptation form in recycling networks. There are given examples of design of some specific systems of a recycling at different levels of localization of cycles and applications of ekologo-logistic audit for an assessment of their efficiency. The report notes that global experience of scientific researches and practical applications of a recycling is in a little demand in Russia. Designing of recycling networks has to become the instrument to influence the plans of a sustainable development both in industrial and society sectors.

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THE STRATEGY OF CHEMICAL ENGINEERING DEVELOPMENT IN RUSSIAN FEDERATION

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There are three main tasks of modern chemistry. The first – to fill the market the most cost-effective products: polymers, fibers, composite materials, fertilizers and pesticides. The second task is to create new classes of products: catalysts, chemical materials for electronics, new composites, smart materials, a new type of drug. This is a real intellectual chemistry when using the latest knowledge from different fields, we get the best product at minimal cost. Finally, the third task is to try to move the processes as much as possible to using the forces of nature, whether photosynthesis, biomass, water protection and so on.

In the old days, we were ahead of other countries in the power unit of production. This key indicator – the unity of the material and energy balance – defines the entire economy. With a decrease in capacity, reduced production yield and increased waste and the specific energy consumption. Today, we are on average ten times losing the power of world production. Even our best plant for the production of polymers in Budennovsk gave 350 thousand tons per year, with the global index of one million tons.

We have excellent professionals. But it refers to the old school engineers and employees of enterprises having a wealth of experience. A new generation of engineers is weak. Today, manufacturers are unhappy with the quality of professionals who come to them after high schools. Without proper equipment of laboratories in universities, we can not move forward.

NANO-OBJECTS IN CATALYSIS: WHEN THE SMALLEST BECOMES THE MOST EFFICIENT

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Catalysts have been for long time considered as the first examples of "nano-designed" materials since the majority of them consist of nano-sized particles of active component supported over high-surface-area solids. Very often nanoparticles (NPs) of metals (Me) are the active component responsible for the catalysis. This is related to the unique properties of NPs which are intermediate between those of Me atoms and Me bulk. The surface structure and the electronic properties of Me NPs change strongly in the range of 1–50 nm. Therefore, the catalyst activity/selectivity may also be sensitive to the Me NPs size change – the effect known as "size-sensitivity" of catalytic reactions. Moreover, the shape of Me NPs also controls the surface atoms which are representing the active sites. This effect is known as "shape-sensitivity" of catalytic reactions.

Advances in colloidal methods for the synthesis of Me NPs with controlled shape and size allow nowadays an exciting opportunity of creating a catalyst "on demand" having an optimized active component in terms of shape and size. Moreover, these NPs can be deposited over supports with optimized micro- and macro-structures allowing an easy access of the reactants to the active sites without any diffusion limitations.

The conjugated approach of an optimized active phase and the structured support is called "*Rational catalyst design*". It spans over several levels of scale and complexity and will be exampled by few case studies during the lecture.

MODULAR LIPID VECTORS FOR GENE DELIVERY

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Gene therapy as the feasible alternative to the conventional medicine implies eliminating the cause of a disease by introducing therapeutic nucleic acids (DNA, RNA, antisense oligonucleotide or siRNA) into a target tissue. Cationic lipids and liposomes are attractive systems for gene delivery. However, their efficiency in a biological environment is often limited or reduced by the interaction with several extra- and intracellular barriers.

In order to increase gene transfer into eukaryotic cells modular non-viral vectors were proposed. These vectors formed by therapeutic nucleic acids and liposomes modified with functional modules that mediated environmental interactions and intracellular traffic to overcome various barriers. Modular vectors should be capable to form stable complexes with nucleic acids, to provide minimal cytotoxicity and to release nucleic acids into target site. Functional modules may increase vector stability in the extracellular milieu and target to specific cell type. Some bioactive groups can be inserted into vectors to facilitate release from endosomes and nuclear transfer. The preparation of modular lipid vectors for gene delivery and their biological activity will be discussed.

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CHLORINE-FREE METHODS OF SYNTHESIS OF ORGANOSILICON POLYMERS IS THE BASIS FOR THE REVIVAL OF SILICONES PRODUCTION IN RUSSIA

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The changes in the model economical development in Russian on the last two decades coincided with dramatic changes in world silicones market. The end of the so called cold war has opened wide perspectives of silicones technologies spreading among many of countries which were never involved to this activity before. This tendency, together with reorientation of chemicals producers towards renewable sources of starting materials, led to the stable increasing of silicones production on world market. In contrast to this tendency production of silicones in Russian dramatically dropped down.

Having in mind, that application of silicones still demand variety of products for many branches of Russian industry simple analysis showed practically full substation of Russian production by imported from abroad. The new plants created in China, Korea and other countries makes very hard any concurrence not only on world silicones market but in Russian market as well.

The only chance for Russian producers to get back the main share of Russian silicones market is invention the new generation of processes of silicones production. As such a case chlorine free production of silicones could be considered. In this paper the processes of the processes of alkoxysilanes based silicones preparation will be considered.

The tasks are standing a front of silicones community of Russia will be discussed and the prospects in creation of the next generation of silicones production will be presented. The situation with silicones production in Russia in our opinion should be considered as a typical for many others branches of chemical products. Therefore the “silicones project” could be considered as a model in overcoming of technological regress observed in last 20 years in some specific areas of chemicals production.

ADVANCED OXIDATION PROCESSES IN SOLUTION OF ENVIRONMENTAL PROBLEMS

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The conceptual regulations of the theory of sustainable socio-economic development provide the creation of resource-saving environmental friendly production, the basis of which are effectively operating resource-saving water chemical processes of industrial plants. It is generally known that textile production is extremely water-retaining and power-consuming. Therefore the problem of resource-saving chemical process analysis and synthesis (designing) of textile plants is of great importance.

The methodology of designing of resource-saving water-use chemical processes of textile plants have been evolved. The environment-oriented analysis of bleaching, dyeing, printing, top (final) finishing shops of large textile enterprises of Central, Volga, South Federal Regions of Russia and of Hubei, Guangdong, Fujian Provinces of China was carried out. The main goal was to design the water-recycling systems on the basis of processes thermodynamic analysis and purified wastewater re-use. So, one of the important step of our research was to investigate the efficiency of various wastewater treatment methods aimed at possibility of treated water re-use. Eventually, it was proved, that the most effective for this purpose are physicochemical advanced oxidation processes (AOP): electrocatalytic destruction, catalytic destruction with strong oxidizing agent presence, catalytic destruction oxidation combined with coagulation. Transition and other metals compounds as catalysts have been used in our research. Hydrogen peroxide and some other chemical compounds were examined as strong oxidizing agents. The mentioned above methods were realized in homogeneous and heterogeneous modes concerning the catalysts, toxic contaminants and treated water aggregate state. Particular sorts of criterion toxic contaminants – various types of dyes and surfactants in water medium have been examined as the objects for destruction aimed in decolorization and detoxication.

Technological advantages of AOP sewage treatment are high efficiency, relative economy, small amount of reagents demand and the absence of sludge in wastewater treatment process. However, despite of the universality of these methods, it was necessary to study in details the conditions of its practical realization. The destruction processes of particular sorts of dyes and surfactants in modeling and textile factories real sewage composition and flowrate conditions have been studied in order to establish the operating characteristics and constructional parameters of processing equipment. We’ve investigated the influence of such parameters as contaminant’s nature, medium pH, temperature, flowrate, sewage composition, electrical action demand, catalytic and sorption properties of catalysts on the efficiency rate of sewage purification process. The kinetic data of oxidation destruction processes of various dyes and surfactants have been obtained. For example, the rate of toxic contaminants concentration reduction while using electrocatalytic metod submits to the second-order equation. The mechanism of pollutants destruction processes was established.

As a whole, it was shown that AOP studied are very perspective in the practice of textile production wastewater treatment. The efficiency rate (destruction degree) of most dyes and surfactants in general is within 70–95%.

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REGULARITIES OF UTILIZATION OF THE REACTIVE OLIGOMERS FOR SPORTING AND ROOFING COVERINGS

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The results of complex investigations, dedicated to the development of organic oligomer derived compositions are summarized in the present communication. The particular features of the above mentioned oligomers are their molecular weights, ranging from 1000 to 5000, accompanied with the presence of epoxide, hydroxyl, carboxy and isocyanate reactive functionalities.

The possibility of hardening of these oligomers for the production of the new generation coverings is demonstrated. It may be achieved in several ways. They are: amine hardening of the oligodienurethanediepoxydes; polyisocyanate hardening of the oligodiendiols and oligoesterpoliols (*via* the one-step urethane-formation); hardening of the oligoester-isocyanate forpolymers by treating them with air moisture and polyfunctional alcohols. The relationships between the complex of physicochemical features of the starting compounds (the nature of the reactive groups, molecular characteristics of oligomers, composition of the hardening and catalytic systems, temperature and concentration parameters together with the starting oligomer composition) and properties of the resulting polymer materials (rheological properties, kinetics of hardening, peculiarities of the net-formation, elastoplastic characteristics and other exploitation properties) are discussed.

The possibility of formation of the coverings based on free injection molding materials discloses the “know-how” of the present invention. Meanwhile, chemical hardening is carried out at the outside temperature, allowing the formation of the surface adhesion bound monolith carpet directly in the place of installation. Development of the series of coverings, agreeable to the standards and regulations of the International Association of Athletics Federation (IAAF), International Handball Association (IHF), Fédération Internationale de Basketball (FIBA) and many others, is the main achievement of this work. The possibilities of practical introduction of the above mentioned compositions in sporting and civil construction is illustrated.

HIERARCHICAL SUPERHYDROPHOBIC SURFACES ON POLYMERS

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Structural hierarchy is a common phenomenon in Nature. It is the key to many biological systems where structural strength has to be combined with special functional properties. An example of such property is hydrophobicity on some plant and animal skins. Superhydrophobic surfaces repel water and make them self-cleaning. The fabrication of superhydrophobic surfaces on polymers has been the topic of many studies since there is a wide range of applications for such surfaces in everyday life. The practical use of the modified polymer surfaces is, however, limited by the poor mechanical durability of the surfaces. The superhydrophilicity is typically based on hierarchical micro-nanostructures on the surface, which minimize the contact of the water droplet. Nanostructures are easily wiped out with mechanical abrasion making the surface less hydrophobic. The wear resistance has been in some studies enhanced with coating techniques or with special structure design but truly durable superhydrophobic polymers have not found their way to commodity markets. In the present work durability of the superhydrophobic surfaces has been improved by using sacrificial structural features on the polymer surfaces. The key is in the creation of hierarchical surface structures at different length scales while protecting delicate nanostructures. The use of structural hierarchy and structure protection will be discussed.

MODIFICATION OF POLYMER FRICTION

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Thermoplastic polymers are nowadays widely used in technical applications and they are increasingly replacing the conventional materials such as metals and ceramics in machine parts owing to their low weight and good processability. In mechanical parts the friction is a very important phenomenon that has to be considered. Polymers already as such have rather low friction coefficients. However, there are applications where an extremely low friction and a high wear resistance are demanded of polymer material. Our research has focused on modification of tribological properties of thermoplastic polymers, e.g. polypropylene and polyacetal, with a periodic patterning of the surface. The surface texturing makes possible to adjust the surface pressure in friction in a convenient way. Dynamic friction in sliding of a polymer surface against a steel counter surface has been studied using a pin on disc-type method. The friction measurements were carried out as a function of surface coverage of micron-sized pillar structures, which were produced with injection molding. The micro-scale surface texture has been found in our studies to affect both friction and wear properties of thermoplastic polymers. The sparsely patterned surface enables the trapping of wear particles in gaps of the micro-pillar structure and hence lowering friction and wear. The wear mechanisms of polyacetal and polypropylene in sliding and the role of viscose fiber enforcement in polypropylene friction will also be discussed.

BIOCOMPOSITES BASED ON POLYOLEFINS AND RENEWABLE BIOMASS. PREPARATION AND PROPERTIES CONTROL

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World annual production of about 300 million tons of plastics, of which about 50% goes to landfill after applying. The most widely used polyolefins (over 40%) pertaining to the most resistant to the environment. It has a problem with polyolefins – polymer waste. Consequently, the development of scientific behind for creation and properties control of biocomposites based on polyolefins and renewable biomass is an urgent problem.

Giving biodegradable properties to polyolefins is achieved by adding natural additives, which include a number of industrial wastes. We used various kinds of starches, cellulose, wood flour, soy flour, brewer's grain, flax waste, sunflower husk, birch leaves, banana skin, sodium lignosulfonate, hay, natural rubber and other.

The influence of the structure of synthetic and natural polymers, morphology, composition, scale factor, the presence of compatibilizer and oxidative modification on the biodegradability of plastics produced is determined. Biodegradation, was estimated by the following parameters: 1 – micromycetes growth rate under laboratory conditions (17 different strains) on wort agar medium, on standard solutions and Capek Getchensona, 2 – in a standardized soil in laboratory conditions and in parallel on the range with periodic measurement of physicochemical parameters – change in mass and chemical composition, defects and other.

Found that one of the main factors determining the intensity of growth and development of micro destructor is the degree of accessibility of natural component encased in synthetic matrix.

Environmental aspect is not only that to reduce number of polymer waste, but also to preserve hydrocarbons by partial replacement to renewable natural raw materials. Futhermore, wastes of a number of industries can be used. This opens up the prospect of reduction in products price in comparison with the current ones, which are used now.

SYNTHESIS OF POLYMERIC MICROSPHERES FOR IMMUNOCHEMICAL RESEARCHES

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Heterophase radical polymerization is the most common method of producing polymeric suspensions are widely used in medicine, biology and biotechnology. The main requirements, which in this case must satisfy the polymer particles – a biological, chemical and colloidal stability in physiological fluids, narrow particle size distribution , the formation of a strong bond between the functional groups of the polymer particles and bioligands.

Among synthetic bioligands carriers used for the preparation of highly sensitive diagnostic test systems are especially useful polymeric microspheres with a narrow size distribution over a wide range of diameters. Uniformity of particle size provides a distinct advantage for use in diagnostic reactions, as it allows to accurately determine the area of the carrier protein molecules and to establish the degree of coating antigen or antibody. Furthermore, the uniformity of particle size distribution causes similar nature of their behavior during the biochemical reaction, which facilitates the "reading" of the reaction results.

To the present time principles of synthesis of polymeric suspensions with narrow particle-size distribution in a broad interval of diameters are determined. The main ways of their synthesis is heterophase the polymerization of hydrophobic monomers (styrene, a methyl metacrylate, vinyl toluene, etc.) in absence of an emulsifier (emulsifier-free a polymerization), a suspension, precipitation seed polymerization.

For obtaining particles with functional groups on a surface, carry out an seed polymerization of the functional monomers (keeping hydroxyl-, epoxy-, amino-, aldehydic groups) on particles of a suspension, more often the polystyrene. The seed polymerization of the functional comonomers allows not only to concentrate the polar groups necessary for the further updating of particles on a surface of particles, but also to increase stability of a suspension even at low concentration of an emulsifier.

At each stage of building of polymeric microspheres and their conjugates with a bioligand a necessary request is conservation of their resistance in biological medium, individuality and narrow particle-size distribution.

Such rigid conditions to polymeric microspheres make necessary maintenance at the stage of their synthesis of formation in their interfacial layers of factors, defining their resistance, and monitoring behind conservation of their action at all stages of obtaining of test -system, namely: at a fixation of a bioligand, staining of particles, addings of a special notch, etc.

From these items all stages of formation of tests – systems with use of the polystyrene microspheres obtained by various ways of a polymerization of styrene have been tracked, with the purpose of obtaining the polymeric suspensions responding formulated requests.

The applications of polymeric microspheres to form substrates for cell growth , as carriers bioligands (instead of red blood cells) to create a diagnostic test systems, working on the principle of passive latex agglutination reaction, to the study of phagocytosis are considered.

THERMOCHEMICAL PROCESSING OF ORGANIC WASTE AND POLYMERS

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The methods of energy recovery from renewable biogenic raw materials are of great importance due to limited amounts of natural energy resources, such as oil and gas. Thus thermochemical conversion technology, e.g. pyrolysis, gasification and combustion are studied extensively [1]. Application of biomass as a source of carbon and energy can be considered sustainable since biomass is a CO_2 neutral resource in the life cycle, causing almost zero net emissions of CO_2, which is a primary contributor to the global greenhouse effect.

From the point of view of the simplicity of the process; level of pollutants control and high yield of the final products, pyrolysis is considered to be an efficient way of converting biomass into combustible gases, oil-like liquid products and solid carbon-containing residues [2]. Various feedstocks are available for pyrolysis: from clean biomass to fuel and polymeric wastes containing different amounts of ash, alkaline and emission precursors like N, Cl and S.

In spite of their variety, modern technologies of biomass pyrolysis are far from perfect as a series of problems hasn't been solved (e.g. low yield of pyrolysis oil, blocking of pipe-lines with coal, quick deactivation of the catalyst) [3]. Part of these difficulties can be overcome when applying stable catalytic systems and technologies.

In this work the influence of natural and synthetic aluminosilicates, metal chlorides of iron subgroup on the peat low-temperature pyrolysis and co-pyrolysis of peat with oil-slime and polymeric waste was studied in variety of conditions (t = 350–650ºC, catalyst loading: from 1 up to 30% (wt.)).

The gaseous mixture obtained during pyrolysis was found to consist of carbon monoxide, carbon dioxide, saturated and unsaturated hydrocarbons and hydrogen. CO_2 is incombustible part of the gaseous mixture, thus, its concentration should be decreased in the combustible gaseous mixture.

As a result of peat pyrolysis it was found that in the presence of catalysts the heat of combustion of gaseous mixture noticeably increased from 8.52 up to 23.88 kJ/mol (Figure 1), which was due to the higher content of lower hydrocarbons. Yield of methane increased in 1.4-1.7 times, ethane – in 1.5-1.9, ethylene – in 2.2-3.4 and propane in 1.8-2.4 times.

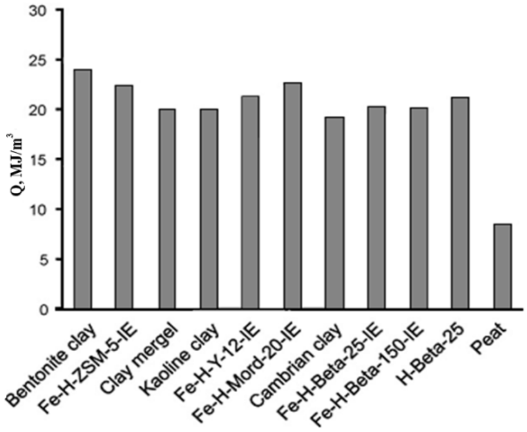

Figure 1. The heat of combustion of the gaseous mixture obtained during the peat pyrolysis.

Bentonite clay was found to be the most active catalyst of peat pyrolysis. The highest heat of combustion (23.88 MJ/m^3) was reached at 460°C. In the case of non-catalytic peat pyrolysis the heat of combustion was only 8.52 MJ/m^3. The average value of the specific heat of combustion was higher approximately by 2.6–2.8 times in comparison with the data obtained for non-catalytic process.

Co-pyrolysis of peat and oil-slime in the presence of bentonite clay resulted in increase of gaseous product weight from 18 up to 26% (wt.), and liquid fraction – from 45 up to 55% (wt.) in comparison with precalculated value. Besides, the use of metal-containing alumosilicate (bentonite clay) allowed obtaining higher concentration of C_1-C_3 (up to 10–20%) in gaseous mixture.

Iron sub-group metal chlorides were used as the catalysts of polymeric cord co-pyrolysis with peat. The choice of iron sub-group metal chlorides is based on the catalytic activity of metal cations in the processes of organogenic raw materials pyrolysis. Positive effect is due to the acceleration of reactions of olefin C–C bond destruction with the formation of hydrogen, low molecular weight alkanes and alkenes. The catalytic activity (degree of the substrate conversion) increased from iron to nickel ($FeCl_2 \rightarrow CoCl_2 \rightarrow NiCl_2$). Nevertheless such dependence of the activity does not affect the gaseous hydrocarbons formation as in the case of $CoCl_2$ the highest volume of gaseous hydrocarbons was observed. Cobalt chloride was the most selective catalyst possessing the intensive formation of both gaseous hydrocarbons and liquid fraction during the pyrolysis. Though the weights of gaseous and liquid products were rather close for $NiCl_2$ and $CoCl_2$, the use of $CoCl_2$ was effective for the obtaining of combustible gases with higher calorific value

The use of co-pyrolysis of peat, polymeric waste and oil-containing waste allows increasing considerably the rate of pyrolysis processes with the production of gaseous and liquid fuels. It was found that the use of catalytic systems does not only decrease the pyrolysis temperature but intensifies the processes of refining and ennobling of low-grade natural raw material.

Acnowledgments

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NEW APPROACHES TO THE CREATION OF EXTRACTIVE DISTILLATION TECHNOLOGY

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Distillation is one of the most widely used industrial methods in the separation of multicomponent mixtures. This raises the problem of flowsheet optimization with energy consumption decreasing. From this standpoint, of great interest are flow sheets with the partially thermally coupled columns (PTCDS) which thermodynamic efficiency lies between the simple and Petlyuk columns. We proposed the methods for their creation only some years ago. Those ones are based on the initial graph transformation of the simple distillation columns sequences. The graph-theoretical approach may be used not only for the zeotropic but also for the extractive distillation flow sheets construction. We proposed such method for extractive distillation flow sheets construction and supplemented it with the graph-theoretical approach for their transformation to partially thermally coupled extractive distillation system (PCEDS).

Recently PCEDS are applied for saving energy. Power consumption reduction by PCEDS differs considerably for the various mixtures up to ~30%, and only by ~ 4.7%. Until now it was unclear why some cases the application PCEDS significantly reduces power consumption, and the other practically gives no effect. Therefore, we carried out a systematic study of the dependence energy consumption reduction by PCEDS on various factors of the process.

We carried out the estimation of effectiveness of PCEDS application for separation of seven binary mixtures with different initial composition and various entrainers (E): acetone – chloroform (E – DMFA), acetone – methanol (E – DMFA, water), allyl alcohol – allyl acetate (E – ethylene glycol), isobutyl alcohol – isobutyl acetate (E – butyl propionate, DMFA), methyl acetate – methanol (E – ethylene glycol), ethyl acetate – ethanol (E – DMSO, propylene glycol) and methyl acetate – chloroform (E – DMFA, ethylene glycol, DMSO). We found the correlation between reflux ratios in the entrainer regeneration column and energy consumption decreasing at PCEDS (Fig. 1).

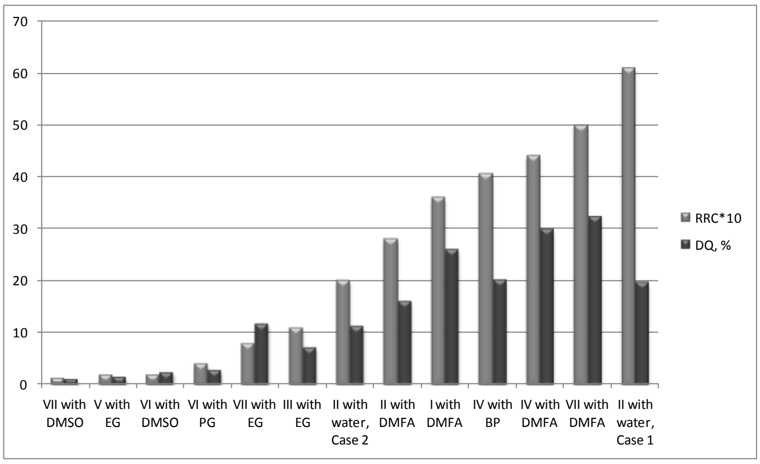

Fig 1. Reflux ratio in entrainer recovery columns (RRC) and reduction of energy consumption by using PCEDS for different mixtures separation.

The investigation gave us an ability to formulate the criterion for evaluation of PCEDS energy efficiency for binary azeotropic mixtures separation.

MODELING OF MEMBRANE MASS-TRANSFER PROCESS ON THE BASE OF NONEQUILIBRIUM THERMODYNAMICS APPROACH

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The aim of the lecture is a discussion of some opportunities of nonequilibrium thermodynamics for the application to membrane processes. The description of membrane systems is a classical task of general and nonequilibrium thermodynamics, e.g. osmotic equilibrium as a case of membrane equilibrium. Nonequilibrium membrane systems have more significance because of numerous practical applications. For example in the case of pressure-driven membrane processes the trans-membrane transport should be considered as non-equilibrium process. Such processes – reverse osmosis, ultrafiltration, microfiltration and others – have a wide range of application, including water treatment. Various membrane processes are accompanied by concentration and partial pressure gradients that also determine non-equilibrium mode of transport. The description of mass-transfer with the use of the elements of non-equilibrium thermodynamics could be applied both to porous and non-porous membranes. In the lecture we consider the general problems of the modeling on the base of non-equilibrium thermodynamics approach. The examples of modeling of permeation through dense nonporous membranes would be presented for pervaporation (PV) and gas separation.

Nonequilibrium approach for the thermodynamic analysis of membrane processes is well-known. Kedem (1986) was one of the first who introduced elements of nonequilibrium thermodynamics in the theory of PV: the theory was applied for the description of the coupling between fluxes. Unfortunately the further development of the thermodynamic theory of PV was not so intensive and only few works of last decade were based on nonequilibrium thermodynamic approach. The PV usually is considered on the base of “solution-diffusion model” [1]. The same model applies to gas permeation and reverse osmosis in polymer films.

For the fluxes in PV in our works we apply classical phenomenological equations (linear laws). For the small fluxes (usual for the PV) the feed solution can be considered as a system in an equilibrium state. Accordingly the equilibrium data on thermodynamic properties of feed could be used. The sorption (as the initial stage of PV) can be also considered as an equilibrium process if the rate of diffusion through membrane is low. For the approximation of the dependence of permeate composition on feed properties the limited set of pervaporation data should be involved in calculation procedure, first of all for the determination of kinetic coefficients values. The coupling between fluxes is taken into account. The conception of driving forces in mass-transfer in PV process is discussed. Some additional assumptions concerning thermodynamic forces in PV are also considered. For general case of membrane systems some results may be also obtained with the use of classical methods of thermodynamics, such as stability conditions. The opportunities and advantages of the use of thermodynamic inequalities for the description and analysis of membrane systems in general are presented. Particularly the inequalities for the analysis both equilibrium and nonequilibrium stages of membrane processes will be presented.

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STUDIES OF IONIC LIQUIDS USING PHYSICO-CHEMICAL METHODS

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Ionic liquids (ILs) are neoteric solvents. Successful industrial applications of ionic liquids are based on the reliable physical-chemical properties. In recent time a scope of experimental and computational methods for obtaining these properties have been developed in our lab for pure ionic liquids and their mixtures with other solutes.

Pure Compounds

- vapor pressure measurements of **Pure** ILs
- vaporization enthalpies of **Pure** ILs
- energies of combustion of ILs
- enthalpies of formation of ILs in the condensed and gaseous phase
- *first-principles* calculations of ILs, thermodynamic analysis of side processes
- real thermal stability
- surface tension measurement

Mixtures

- activity coefficients at infinite dilution of **Solutes**
- limiting partial molar excess enthalpies of organic **Solutes** in IL
- activity coefficients (IL+ **Solute**) in the full concentration range
- VLE measurements of binary solutions of IL and solvent
- LLE-Liquid-Liquid equilibrium measurements
- solubility of gases in IL
- enthalpies of IL synthesis reaction

These methods will be discussed in aspects of their relevance for the practical applications of ILs.

Section 1

Theoretical Bases of Chemical Engineering

OLIGOMERIZATIN OF 1-OCTENE OVER MESOPOROUS ALUMINOSILICATES

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The oligomerization of 1-octene over acid catalysts is an important industrial way for the production lubricants [1]. Traditionally oligomerization of 1-octene is carried out by Lewis acids such as $AlCl_3$ and BF_3. A major problem associated with the technology is the use of corrosive liquid phase acid mixture, responsible for the generation of large amounts of wastes, which are costly to treat. An alternative could be the substitution of Lewis acids with mesoporous aluminosilicates.

In this paper presented the results of oligomerization of 1-octene over mesoporous aluminosilicates. Mesoporous aluminosilicates with various chemical compositions have been prepared by sol-gel method. The precipitates were formed by adding conc. aqueous ammonia to an ethanol solution of $Al(NO_3)_3{\cdot}9H_2O$ and $Si(OC_2H_5)_4$ (TEOS). Their porous properties investigated by nitrogen gas adsorption, transmission electron microscopy (TEM), small angle X-ray scattering (SAXS), and ^{29}Si and ^{27}Al magic angle spinning nuclear magnetic resonance (MAS NMR). Fig. 1 shows the pore size distribution of the aluminosilicate with SiO_2/Al_2O_3=20.

The reactions oligomerization of 1-octene over mesoporous aluminosilicates (SiO_2/Al_2O_3=20÷120) was carried out at a temperature of 100÷200 °C in the presence of 10÷20% wt. and atmospheric pressure in a autoclave reactor.

It was found that the main products of the reaction oligomerization of 1-octene over mesoporous aluminosilicate catalyst are oligomers with a degree of oligomerization n = 2-4.

Conversion octene studied conditions reaches 100%, the selectivity of dimers – 40÷55% trimers – 25÷30%, tetramers – 5÷10%. Fig. 2 summarizes the results obtained in the liquid phase oligomerization of 1-octene over the mesoporous aluminosilicates .

Investigated the influence of physico-chemical characteristics derived aluminosilicates and oligomerization conditions for the conversion of 1-octene and the selectivity of the formation of oligomers.

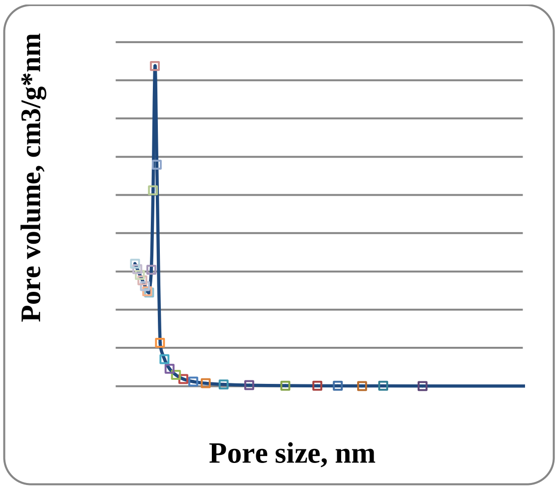

Fig. 1

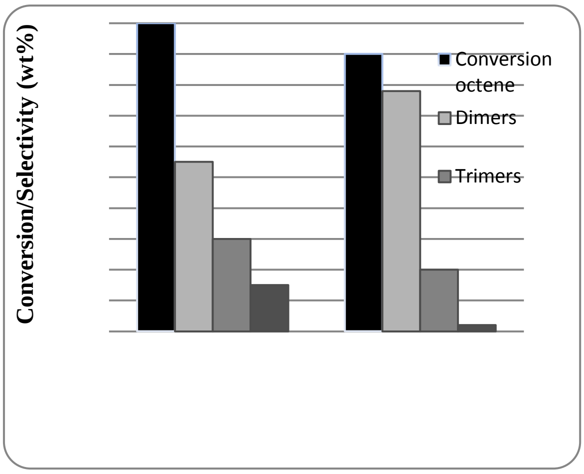

Fig. 2

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SELF-ASSOCIATION THERMODYNAMIC PARAMETERS OF SECONDARY HYDROPEROXIDS IN SOLUTIONS

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The self-association of secondary ethylbenzene (EBHP), sec-butyl (SBHP) and diphenylmethyl (DPMHP) hydroperoxides in solutions of the n-decan, carbon tetrachloride (CCl_4), chlorbenzene was investigated by IR-spectroscopy (3100 - 3700 cm $^{-1}$, 20-80^{0}C) It is established, that in solutions at concentration <0,6 mol/l hydroperoxids exist as a mix of monomers and hydrogen-bonded dimers and trimers. Processing of a package of IR-spectra of hydroperoxids solutions with various concentration determines concentrations of monomers and self-associats, then dimerisation and trimerisation equilibrium constants. On temperature dependence of equilibrium constants (Vannt-Goff equation) the thermodynamic parameters of self-association are calculated.

Equilibrium constants and thermodynamic parameters of hydrogen bond formation in SBHP, EBHP, DPMHP solutions

HP	Solvent	K_D^{20}, l/mol	K_T^{20}, (l/mol)^2	$-\Delta H_D$, kJ/mol	$-\Delta S_D$, J/(mol·K)	$-\Delta H_T$, kJ/mol	$-\Delta S_T$, J/(mol·K)
SBHP	n-$C_{10}H_{22}$	2.7	5.4	22.5	67.0	31.6	91.8
	CCl_4	1.0	2.2	14.3	47.9	19.6	59.3
	C_6H_5Cl	0.8	1.6	13.3	46.9	18.5	58.1
EBHP	n-$C_{10}H_{22}$	3.2	21.9	19.6	56.0	26.8	63.5
	CCl_4	2.4	4.4	12.9	36.1	18.4	49.7
	C_6H_5Cl	1.1	2.1	11.0	36.2	15.9	47.1
DPMHP	n-$C_{10}H_{22}$	1.2	-	21.7	71.1	-	-
	CCl_4	1.0	4.1	16.2	54.2	20.3	56.5
	C_6H_5Cl	0.7	1.4	11.6	41.6	16.7	53.5

Apparently from the table, the maximal values of thermodynamic parameters di- and trimerisation are observed in n-decan solutions who for this reason should be counted the inert solvent which is in any way not influence on the self-association process. Decreasing of enthalpy in CCl_4 and chlorbenzene is caused solvation of monomers by solvents.

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KINETIC MODEL OF CYCLOHEXENE HYDROCARBOMETHOXYLATION PROCESS CATALYSED BY PALLADIUM-DIPHOSPHINE COMPLEXES

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At single-factor experiments the kinetics of cyclohexene hydrocarbomethoxylation catalysed by $Pd(OAc)_2$ / rans-2,3-bis(diphenylphosphinomethyl)norbornane (TBDPN) / p-toluenesulphonic acid (TsOH) system were studied at 378 K. First-order reaction rate dependences were established for the cyclohexene and $Pd(OAc)_2$, while non-monotonic rate dependences were determined for the TBDPN and TsOH concentrations and P_{CO}. The reaction was shown to follow first order kinetics when the CH_3OH concentration was below 0.4 mol/L, however, the reaction rate slowed upon a further increase in the methanol concentration. The obtained results were interpreted by considering a hydride mechanism supplemented with ligand exchange reactions, which decrease the activity of the catalyst, and with hydride complex annihilations by TsOH, resulting in the complete loss of catalytic activity. Treatment of the proposed mechanism using the quasi-equilibrium concentration method gave an equation for the reaction rate that was consistent with the experimental data:

$$r_0 = \frac{kC_{cat}P_{CO}[ol][TsOH][CH_3OH]}{\left\{1 + a[CH_3OH][TsOH] + bP_{CO}^2 + c\frac{P_{CO}^2[TsOH]}{[TBDPN]} + d[TBDPN]^2 + e\cdot[TsOH]\right\}},$$

where C_{cat} is the concentration of the initial form of the catalyst $Pd(OAc)_2$, [ol] is the cyclohexene concentration; a, b, c, d, e, k are the parameters demonstrating the contribution of different palladium forms into the total balance of catalyst.

The estimation of the parameters of equation for the initial reaction rate on the base of all experimental data with using MS Excel 2010 gives the values presented in the following equation:

$$r = \frac{C_{cat}P_{CO}[ol][TsOH][CH_3OH]}{\left\{\begin{matrix}(1.47\pm 0.18)\cdot 10^5\cdot[CH_3OH][TsOH] + (2.26\pm 0.41)\cdot 10^{-11}\cdot\frac{P_{CO}^2[TsOH]}{[TBDPN]} + \\ + (5.77\pm 0.25)\cdot 10^6\cdot[TBDPN]^2\end{matrix}\right\}}\left[\frac{mol}{L\,min}\right],$$

where P_{CO} is CO pressure [Pa].

The receiving kinetic model is the base for estimation and optimization of methyl cyclohexanecarboxylate synthesis reactor.

The reported study was partially supported by RFBR, research project No. 14-08-00535.

QUANTUM-CHEMICAL STUDY OF THE ELECTRONIC STRUCTURE OF SATURATED AND UNSATURATED N-HYDROCARBONS

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Optimization of technological processes in chemical industry requires a preliminary study of all physical-chemical properties of the components of these processes. However, the definition of the compound properties by experimental methods is often difficult because of various reasons; therefore the methods of mathematics forecasting should be employed.

Theoretical modelling in physical chemistry has to base on quantum mechanics. One of the most powerful modeling tools is the "quantum theory of atoms in molecules" (QTAIM) [1] allowing to break a molecular electron density in "topological" atoms and explore the intramolecular and intermolecular interactions. This gives the opportunity to identify and prove the regularities that can be laid in the basis of the quantitative correlations "structure - property" and "structure - activity" when methods of forecasting of physical-chemical properties are building.

In this paper the study of electronic structure of *n*-alkanes, *n*-alkenes and *n*-alkynes homologous series i.e. $CH_3(CH_2)_nR$, where $n = 0 \div 8$, and terminal fragment $R = CH_3$, $CH_2 = CH$ и $CH \equiv C$, was carried out.

The optimization of the compound geometries in studied homological series was performed by program Gaussian 03 with B3LYP/6-311++G(3df, 3pd) [2]. The characteristics of atoms (charge q, energy E, volume V) and critical points of bond paths (electronic density ρ_b, ellipticity ε, Laplacian $\Delta\rho_b$) were calculated using program AIMALL [3]. Properties of atomic groups and fragments were obtained by summing the corresponding characteristics of atoms forming its groups or fragments.

Analysis of charges allowed to express the qualitative scale of electronegativity groups as:

$$\chi(\mathbf{CH_2}) < \chi\ (\mathbf{CH_3}) < \chi\ (\mathbf{CH_2{=}CH}) < \chi\ (\mathbf{C{\equiv}CH}),$$

where $\chi(CH_2)$ is electronegativity of the "standard" CH_2 group.

The studying of the electron characteristics of R showed that the influence of the terminal fragments in *n*-alkenes and *n*-alkynes spreads on the nearest two CH_2, and with increasing of C-C bond multiplicity this influence is growing.

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PRODUCTION OF BIODIESEL FROM SOYBEAN OIL USING HETEROGENEOUS CATALYST

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Nowadays, biodiesel (fatty acid methyl esters, FAME) is considered as an alternative of petroleum based diesel fuel. It is environmentally friendly and renewable energy source, free from sulphur and carcinogen content, and is a non-toxic and biodegradable fuel. FAME is currently produced by transesterification from vegetable oils with methanol in the presence of homogeneous catalysts such as sodium hydroxide and sodium methylate. Although transesterification using a conventional alkali catalyzed process gives high conversion levels of triglycerides to their corresponding methyl esters in short times, the reaction has several drawbacks: it is energy intensive, the catalyst has to be removed from the product, alkaline waste-water requires treatment, which leads a high cost of biodiesel.

Therefore the optimal is to use heterogeneous catalysts. Calcium oxide is one of the most promising heterogeneous catalysts as it has a lower solubility, lower price and availability. However, its transesterification reaction rate is lower compared with homogeneous catalysts. The low catalytic activity of calcium oxide related to the fact that metal oxides absorb water and carbon dioxide from the air with the formation hydroxides and carbonates on the surface. The highest catalytic activity showed a sample calcinated at 600ºC. Hydroxide and calcium carbonate are almost completely converted into CaO at this temperature.

Investigation of the water addition's effect on catalyst activity of calcined at 600ºC calcium oxide found that the introduction of a small quantity of water in the reaction system can significantly increase the catalytic activity of calcium oxide. The yield of FAME ~ 98% has been achieved within 2 h of the process in the presence of water in an amount of 0.2% (wt).

Pretreatment of calcium oxide with methanol can significantly increase the basicity of the catalyst and its activity in the transesterification reaction. OH^- and CH_3O^- groups are formed on the surface by reacting CaO with methanol, therefore to reduce the induction period. Biodiesel and glycerol are formed more quickly in the transesterification reaction. Glycerol is reacted with calcium oxide, causing the significant increase of catalytic activity of the calcium oxide. In order to investigate the glycerin's effect on the catalytic activity of calcium oxide, calcinated at 600ºC, it was activated by methanol with addition of small quantities of glycerol for 60 min at 60ºC immediately before the process. The catalytic activity of the calcium oxide has significantly increased by adding to the initial mixture of glycerol. Yield of FAME of 65% was reached after 60 min of the process after addition of 0.5% (wt.) of glycerol. However, the yield of FAME was reduced by adding more than 1.5% (wt.) glycerol.

The influence of different homogenizers (glycol stearate and glyceryl monostearate) on the catalytic activity of CaO, calcined at 600ºC was investigated for homogenization of the initial mixture of methanol and soybean oil. An increase of the initial rate of the reaction was observed after the addition of glycol stearate and glycerol monostearate to the reaction mass. Yield of biodiesel of 55% was obtained after 60 min.

In conclusion, the activity and stability of the calcium oxide was investigated in the transesterification reaction of soybean oil with methanol. The catalytic activity of the calcium oxide is only slightly decreased after the 10 cycles.

Pt/γ-Al_2O_3 AS AN EFFICIENT CATALYSTS FOR GAS-PHASE DEHYDRATION OF GLYCEROL TOWARDS ACROLEIN

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Acrolein is used for the production of the acrylic acid, methionine, 1,3-propanediol and other chemical products. Acrolein is currently produced by the oxidation of propylene using multi component mixed oxide catalysts [1].

On the other hand, the chemical industry is increasingly used of renewable resources due to the high cost of mineral resources and stricter sustainability requirements for chemical plants. In recent years, the increasing production of biodiesel has resulted in a price decline of crude glycerol, making aqueous glycerol an attractive compound for the synthesis of fine and crude chemicals.

Therefore, the use of glycerol as a starting material becomes economically and environmentally feasible. Catalytic conversion of glycerol to acrolein by a dehydration reaction could be an important route for using glycerol resources and could offer a sustainable alternative to the present acrolein technology based on propylene [2].

Dehydration of glycerol is carried out in liquid or gas phase. Three types of catalyst allow the reaction to run successfully: zeolites, heteropolyacids and metal oxides. However, the main problem remains rapid catalyst deactivation due to carbon deposition. Up to now, no catalyst has had a half-life of more than a few days, which is of course not sufficient for commercial applications. The catalyst deactivation occurs due to extensive coke deposition on its surface, and attempts to limit the rate of coking by adding inert gas and modifying of the catalysts by introducing of expensive additives (e.g., Nb_2O_5, rare-earth elements) have not been convincingly successful. Furthermore, in most published studies dehydration of glycerol was carried out on the catalyst powder (particle size less than 1 mm), which may cause some technical problems in industrial application and will increase the cost of production of acrolein and makes these methods practically unapplicable.

We have examined a new type of catalyst systems based on γ-Al_2O_3 in the gas-phase dehydration of glycerol. Many of these commercial catalysts show excellent catalytic performance. Not only its catalytic performance, but also the low price of gamma alumina increases its attractiveness as catalyst carrier.

It was demonstrated that γ-Al_2O_3 catalyst exhibits high initial activity, with a glycerol conversion of 100% at 74% acrolein selectivity after 10 h. However, the acrolein selectivity was equal to 50% at 75% conversion of glycerol over A-64 after 50 h.

It has been found that doping γ-Al_2O_3 with Pt improves catalyst stability to deactivation. Pt/γ-Al_2O_3 commercial catalyst (AP-64) showed the highest catalytic activity after 50 h of reaction with an acrolein selectivity of 65% at a conversion of glycerol of 90 % and a reaction temperature of 375ºC under ambient pressure. Based on these results, Pt/γ-Al_2O_3 catalysts appear to be most promising for gas phase dehydration of glycerol.

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MOLECULAR DESIGN OF METAL-COMPLEX CATALYSTS OF REACTIONS WITH PARTICIPATION OF FRAME CARBOCYCLIC COMPOUNDS

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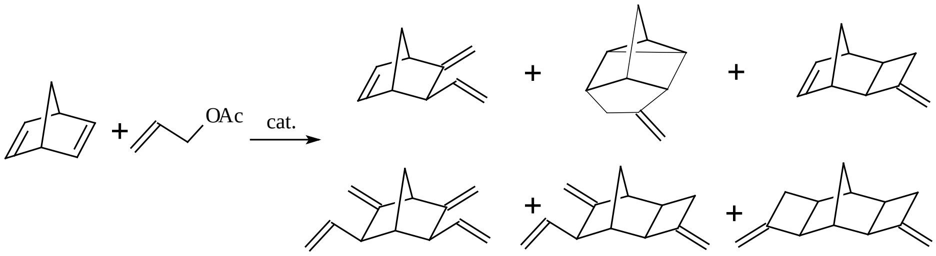
Catalytic processes with norbornadiene (NBD) participation offer exceptional opportunities for synthesis of a wide range of hard-to-reach polycyclic hydrocarbons. Effective application of such synthetic techniques as homodimerization, sodimerization and alternative allilation of norbornene and norbornadiene large number allows to develop a unique strategy of carbocyclic structures obtaining with methylene, vinyl and methyltrichlorosilane fragments.



The problem of selectivity in multi-path reactions with NBD participation and its derivatives are of critical importance. On the example of NBD and norbornene allilation reactions it was shown the possibility of speed and selectivity regulating of various levels. It was investigated in detail the ways of nickel and palladium catalysts formation, by spectral methods it was identified key intermediates, installed kinetic regularities, proposed consistent mechanisms. It was carried out quantum-chemical modeling of processes with participation of NBD. It was established the factors influencing on the reaction directions and allowing quantitatively to receive individual stereoisomers. Selectivity and the number of cycles depend on the composition of catalytic systems and the effective charge on metal. It was synthesized a series of new unsaturated compounds, having a set of double bonds with various reactionary ability and which interest to get modified rubbers.

It was performed the comparison of homogeneous and heterogeneous metal-complex catalysts application efficiency, was revealed common features and differences in the reaction mechanisms.

The work was supported by RFBR (grant No. 14-03-00419-a).

THE SEPARATION OF TERNARY SYSTEM ISOPROPYL ALCOHOL – 1,2-DICHLOROETHANE – WATER IN RECTIFICATION COMPLEX WITH FLORENTINE VESSEL

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Isopropyl alcohol (ISA) – 1,2-dichloroethane (D) – water (W) is a mixture of solvents generated in the production of vitamin «A». The systems diagram of vapor-liquid equilibrium is characterized by the presence of three binary and one ternary azeotrope and belongs to the class 3.3.1-2 (figure 1a). Components 1,2-dichloroethane and water are limited soluble in each other, therefore there will be two-phase splitting area of a closed type on the splitting diagram. All tie-lines below the limit tie-line (shown by the dashed line), allow to realize the principle of redistribution of concentration fields for the separation of the mixture in three-column rectification complex with florentine vessel (figure 1 b).

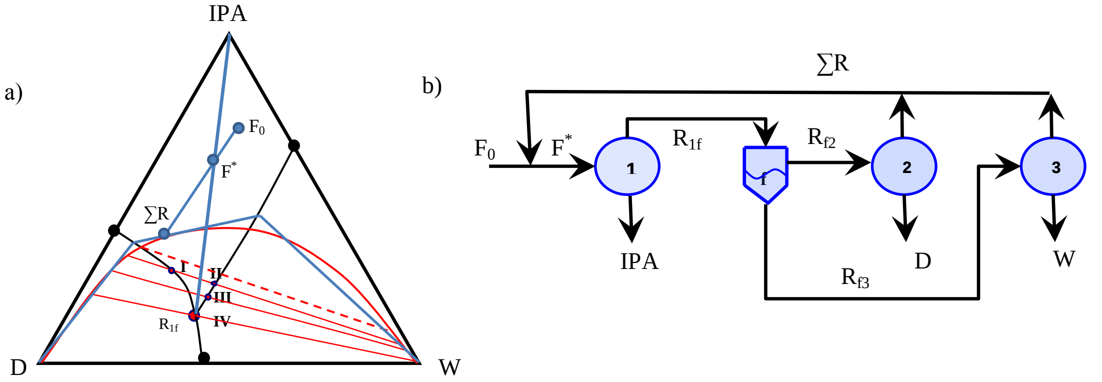

Figure 1. The diagram of phase equilibrium of ternary system IPA – D – W (a) and principal technological separation scheme (b). The material balance lines are shown for case IV.

Composition of the stream R_{1f}, which may belong simultaneously to any tie-line, lying between the limit tie-line and tie-line passing through the ternary azeotrope, and any of separatrices generated by binary homogeneous azeotropes, is decisive in technological scheme material balance calculation. Material balance was calculated for the four positions of R_{1f} (figure 1a, cases I–IV) and operating parameters of rectification columns work providing for the separation of the components of a purity 0.99 mol. frac. were determined. The number of theoretical plates in all schemes ranged from 20 to 30, reflux number from 1 to 7. The choice of a distillate point of first column influences the distillate stream in the second and third column, and the total recycle stream (table 1).

Table 1. Energy consumption for separation at different location of R_{1f}

Location of R_{1f}	I	II	III	IV
∑R, kmol/h	1.1466	1.2803	0.4369	0.2069
Energy consumption, kW	695.57	488.23	123.82	50.2

This interrelation is principal when the nonlinearity of separatrices is observed, which will define the recycle streams and overall energy costs for the principal technological scheme. The preferable case for system separating is the IV-th.

NATURAL SCALES IN USE

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Analytical solution has always prevailed through the history of engineering. While difficulties of the equations are growing, the number of numerical solutions is also going up. One could tell that numerical is not exact, but approximate solution. Besides, information about a process is lost in numerical solution due to the impossibility of revealing relations between variables. But in chemical technology it is agreed that numerical solution is usually better than the analytical one if in the process of numerical solution all effects are taken into account.

Furthermore there is an alternative to both kinds of solution. One can receive numerical information and the basic links without any solution by using methods of so called generalized analysis [1]. There are three different methods described by authors of [1] that are commonly known. However, only one extremely rarely used method called Natural Scales [1, 2] will be analyzed and the application will be provided.

Results of analytical or numerical solutions represent a set of relations between parameters and/or value of all parameters in each part of the system. This information is not necessary for the projection of the equipment, as it doesn't help find optimal parameters. In other words, if there is a solution to equations which describe the process, it is possible to get a large number of new tasks for optimization in order to find the optimal parameters of the process.

In its turn, Natural Scales Method presupposes finding only dimensioned values of variables. This method reminds of similarity theory; however, the nondimensionalization of the parameters occurs in a slightly different manner. The result represents not only the relations F =F(x, y, z), but also the values of so called natural scales.

These values provide sufficient amount of information which is necessary for a process design, as they show material alteration value of the function [1, 2]. Many examples of practical tasks' solutions were described in [2]. In this work there is also contain one.

In the new technology the task have appeared to design the processes and facilities for the reaction. Co-product in mentioned one is acetic acid is to be removed by evaporation. There are 3 different problems about this task. It will be show how natural scale works only on one of this - the problem of removal bubbles out of the reaction zone.

Each bubble has it's acceleration: $ma = \sum F_i$. Each bubble has two impact forces:

$$F_1 = mg = (\rho_{\text{ж}} - \rho_{\text{г}})g\frac{\pi d^3}{6};$$

$$F_2 = \xi\frac{\rho_{\text{ж}}}{2}(\vec{W} - \vec{U})|\vec{W} - \vec{U}|\pi d^2 = \frac{24\nu}{|\vec{W} - \vec{U}|d} * \frac{\rho_{\text{ж}}}{2}(\vec{W} - \vec{U})|\vec{W} - \vec{U}|\pi d^2 = 12\nu\rho_{\text{ж}}\pi d(\vec{W} - \vec{U})$$

$$\begin{cases} \rho\frac{\pi d^3}{6}\frac{\partial^2 z}{\partial \tau^2} = (\rho_{\text{ж}} - \rho_{\text{г}})g\frac{\pi d^3}{6} + \frac{24\nu\rho_{\text{ж}}\pi d^2}{8d}\left(-\frac{\partial z}{\partial \tau}\right) \\ \rho\frac{\pi d^3}{6}\frac{\partial^2 x}{\partial \tau^2} = 12\nu\rho_{\text{ж}}\pi d\left(W(z) - \frac{\partial x}{\partial \tau}\right) \end{cases}, W(z) = \frac{W_0}{H} * z$$

initial conditions

$$x(\tau = 0) = x_0;\ \dot{x}(\tau = 0) = \dot{x}_0;\ z(\tau = 0) = z_0;\ \dot{z}(\tau = 0) = \dot{z}_0;$$

Nondimentionalization would be in form of splitting the parameter into nondimentionalized operators and dimetionlized factor.

$z = z_\# * \hat{z};\ x = x_\# * \hat{x};\ z = \tau_\# * \hat{\tau}$

$$\begin{cases} \rho_{\text{г}}\dfrac{\pi d^3}{6} * \dfrac{z_\#}{{\tau_\#}^2}\dfrac{\partial^2\hat{z}}{\partial\hat{\tau}^2} = (\rho_{\text{ж}} - \rho_{\text{г}})g\dfrac{\pi d^3}{6} - 12\nu\rho_{\text{ж}}\pi d * \dfrac{z_\#}{\tau_\#}\dfrac{\partial\hat{z}}{\partial\hat{\tau}} \\ \\ \rho_{\text{г}}\dfrac{\pi d^3}{6}\dfrac{x_\#}{{\tau_\#}^2}\dfrac{\partial^2\hat{x}}{\partial\hat{\tau}^2} = 12\nu\rho_{\text{ж}}\pi d(\dfrac{W_0}{H} * z_\#\hat{z} - \dfrac{x_\#}{\tau_\#}\dfrac{\partial\hat{x}}{\partial\hat{\tau}}) \end{cases}$$

If we taking into account all effects in this equations all factors should be of same power of 10.

$$\rho_{\text{г}}\frac{\pi d^3}{6} * \frac{z_\#}{{\tau_\#}^2} \sim (\rho_{\text{ж}} - \rho_{\text{г}})g\frac{\pi d^3}{6} \sim -12\nu\rho_{\text{ж}}\pi d\frac{z_\#}{\tau_\#} \sim \rho_{\text{г}}\frac{\pi d^3}{6}\frac{x_\#}{{\tau_\#}^2} \sim 12\nu\rho_{\text{ж}}\pi d * \frac{W_0}{H} * z_\# \sim \\ -12\nu\rho_{\text{ж}}\pi d * \frac{x_\#}{\tau_\#}$$

And initial conditions divided to each other to be proportional to 1 are below.

$$1 \sim \frac{x_0}{x_\#} \sim \frac{z_0}{z_\#} \sim \frac{\dot{x}_0\tau_\#}{x_\#} \sim \frac{\dot{z}_0\tau_\#}{z_\#}$$

The most wanted scales $z_\#$ and $x_\#$, cause they'll give us length of lifting the bubble/ $L = \frac{(3\div5)H}{z_\#} * x_\#$

There are a lot of $z_\#\ and\ x_\#\ and\ \tau_\#$ scales, but only one should be chosen for the whole system.

For example $x_\#$ scale divided from Inertia force and viscosity of the fluid flow, other scales divided for inertia and one of the forces from first equation.

$$x_\# = \frac{72\nu}{d^2}\frac{\rho_{\text{ж}}}{\rho_{\text{г}}} * \frac{W_0}{H} * z_\#{\tau_\#}^2,\quad z_\# = \frac{(\rho_{\text{ж}} - \rho_{\text{г}})}{\rho_{\text{г}}}g{\tau_\#}^2,\quad \tau_\# = \frac{z_\#}{\dot{z}_0}$$

$$x_\# = \frac{72\nu}{gd^2}\frac{\rho_{\text{ж}}}{(\rho_{\text{ж}} - \rho_{\text{г}})} * \frac{H}{W_0}{\dot{z}_0}^2$$

And analytical solution (without taking into account initial conditions) is eq.

$$Z = C_1 + C_2 e^{-\frac{72\nu\rho_{\text{ж}}}{d^2\,\rho_{\text{г}}}} + \frac{(\rho_{\text{ж}} - \rho_{\text{г}})}{\rho_{\text{ж}}} * \frac{gd^2}{72\nu}$$

$$X = C_1 + C_2 e^{-\frac{72\nu\rho_{\text{ж}}}{d^2\,\rho_{\text{г}}}} + \frac{W_0}{H} * z$$

So in both methods results and resources are different enough to prefer natural scales method in most cases.

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SYNTHESIS OF PYRIDINE AND PICOLINES OVER ZEOLITE CATALYST

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Pyridine and substituted pyridines are the important intermediate products for the synthesis of pharmaceuticals, herbicides, metal corrison inhibitors, conventional ligands for the chemical assembly of coordination compounds and surface-active agents [1].

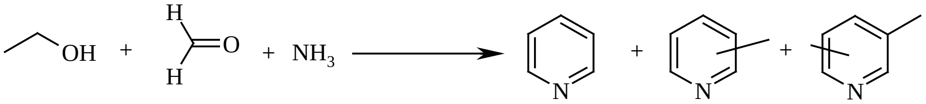
The known methods for obtaining of pyridine and its derivatives co-produce many byproducts and involve heavy coking of the catalyst [1].

In this work, the multi-component reaction of ethanol with formaldehyde and ammonia has been studied under the action of different zeolite catalysts, such as H-Beta (of the structural BEA type), H-ZSM-12 (MTW), and H-ZSM-5 (MFI).

Zeolites NH_4-Beta (BEA) and H-ZSM-12 (MTW) were produced by the public corporation Angarsk Factory of Catalysts and Organic Synthesis. Zeolite NH_4-Beta was transferred into H-form by calcination at 540 ^{0}C for 4 h. H-ZSM-5 zeolite is synthesized at OJSC “Novosibirsk Plant of Chemical Concentrates”.

The reactions of ethanol, formaldehyde and ammonia over zeolite catalyst was carried out at a temperature of 200 – 400 ^{0}C and atmospheric pressure in a tubular fixed-bed reactor. The weight hourly space velocity (WHSV) was varied from 0.5 to 7 h^{-1}. The molar ratio of ethanol: formaldehyde: ammonia varies within the range of 1.0: 0.4-1.1: 1.5 molar.

We have found that under the H-Beta, H-ZSM-5, and H-ZSM-12 zeolite catalysts ethanol interacts with formaldehyde and ammonia yielding pyridine, picolines (2-methylpyridine, 3-methylpyridine, 4-methylpyridine, predominantly 3- and 4-methylpyridine), lutidines (dimethyl-pyridines, mostly 3,5-dimethylpyridine), and more “heavy” compounds as compared to pyridine:



The activity of catalysts evaluated by the degree of ethanol conversion reaches its maximum on the H-Beta zeolite catalyst and diminishes going to H-ZSM-5 and H-ZSM-12 zeolites. The temperature rise from 200^{0}C to 400^{0}C, the decrease in the volume flow rate from 10 h^{-1} to 0.5 h^{-1}, and an increase in the formaldehyde content in the raw feed have been found to increase the conversion of ethanol over zeolite catalyst.

The selectivity of the pyridine formation over H-Beta zeolite reaches its maximum of 49% at 200^{0}C and 2 h^{-1}. The elevation of temperature, the reduced volume flow rate and formaldehyde concentration in the raw mix result in a higher quantity of methylpyridines and “heavy” compounds in the reaction product composition.

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HETEROPHASE HYDROLYSIS OF ORGANOCHLORO(ALKOXY, ACETOXY)-SILANES: ROLE OF REACTIONARY PHASE`S FEEDING BY WATER

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It was previously found that the formation of the polymer chain in the hydrolytic polycondensation (HPC) of diorganodichlorosilanes passes with a great share stepwise assembly, but smaller blockwise (as gomorofunctional condensation (GMFC) of diorganosilandiols) [1]. The reason of this is the nature of the heterophase process which define drawback hydrolyzing agent in the reaction zone and as a consequence, the assembly (forming) of the chain passes through "connection" to the growing chain both monomer molecules R_2SiCl_2 and intermediate $R_2SiClOH$.

The comparative data was given about the assembly of polymer chain for four monomers classes such as $Me_2Si(OH)_2$, Me_2SiX_2 (X = Cl, OR (R = Me, Et, iPr, Bu), $OCOCH_3$). This objective was solved by studying the composition of products in the hydrolysis diorganodialkoksisilanes depending on the ratio of reactants. The main tool for the analysis and evaluation criterion in the oligomer chain was the dependence conversion of the monomer (Xm) vs the conversion of the functional group (X_f) [1]. The GLC method was used to estimate composition of products and nature of chain.

The dependencies of monomer conversion vs functional groups conversion were obtained on the basis of data about the composition of products GMFC $Me_2Si(OH)_2$, HPC Me_2SiX_2. It was established that the share of stepwise assembly oligomeric molecules and the contribution heterofunctional condensation in chain growth rise in a series of reactivity increasing $Me_2Si(OH)_2$ < $Me_2Si(OR)_2$ < $Me_2Si(OCOCH_3)_2$ ≈ Me_2SiCl_2. The dependencies shift Xm = f(Xf) from left to right is usually associated with an increase in the reactivity of the oligomers [2]. We assume that such series of dependencies may be caused by the change in the ratio of the velocities of mass-transfer and chemical reactions, defining a different intensity of "feeding" reaction phase by the water.

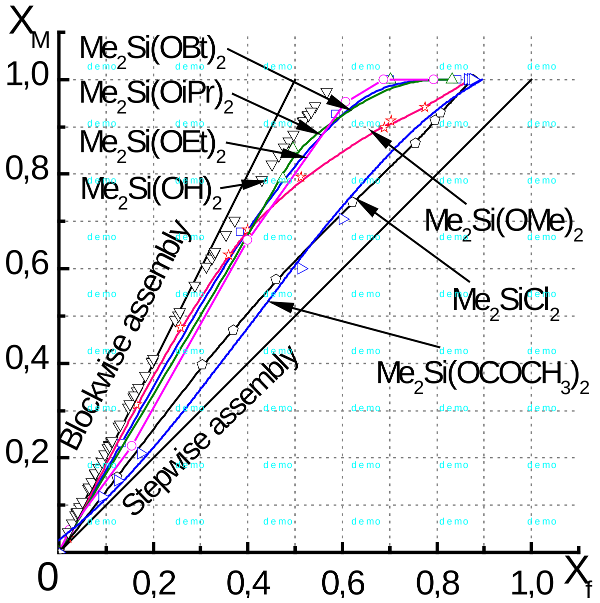

Fig. 1. Depending the conversion of monomer vs the conversion of functional groups in dioxane for GMFC $Me_2Si(OH)_2$, HPC Me_2SiX_2.

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REACTIVE-EXTRACTION PROCESES IN SILICONES PRODUCTION

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The hydrolytic polycondensation of functional organosilanes is an essential process for polyorganosiloxanes producing. Macrokinetic hydrolytic regularities of organochlorosilanes lies in the theory basis of this process1. The main misleading of investigators in the representation of this process that polyorganosiloxanes are formed by homofunctional condensation of hydrolysis products was eliminated. In accordance with the modern classification the hydrolytic polycondensation of R_nSiX_{4-n} (X = Cl, OR; n = 1÷4) is a heterophase combined reactive mass-transfer process, and the mass-transfer plays an important role in creating of the field of reagents concentrations in the reaction phase.

Basic theoretical positions of the hydrolytic polycondensation of RnSiX4-n are:

- Water and R_nSiX_{4-n} are phase-forming components due to the limited mutual solubility;
- R_nSiX_{4-n} is a monomer with a hidden functionality, own monomer for the hydrolytic polycondensation is formed by the hydrolysis R_nSiX_{4-n};
- Layering of systems H_2O – solvent – R_nSiX_{4-n} – $R_nSi(OH)X_{3-n}$ are evaluated by UNIFAC and NRTL.
- The formation of siloxanes goes to mechanism of heterofunctional condensation hydrolysis products due to lack of water in the reaction phase, molecular weight and structure of polymer depend on molar ratio ($m = [H_2O] / [R_nSiX_{4-n}]$) in the reaction zone;
- The control for m is carried out by varying mixing proportion of the reaction system and hydrodynamics2;
- Molecular weight and structure of the polymer is determined by the local phase quasi-equilibrium relatively, which is preceding the rate-limiting step of the process;
- The hydrolytic polycondensation of functional organosilanes is carried out as emulsion or phase boundary method depending on the mutual solubility and reactivity of reagents.

A choice of method depends on the nature of the solvent and reactivity of monomers. In case of high-reactive reagents (organochlorosilanes) for the reagents proportion control in the reaction zone (m) is a common solvent (acetone , alcohols, tetrahydrofuran, etc.). For delivering of water in the reaction zone is necessary to increase the concentration of solvent in the mixing proportion3. The proportion of the velocity of water molecules transportation in the reaction phase (phase adding of water1) and chemical reaction rate is an important factor of the choice of method. It was found that to achieve the same values of m in the reaction phase the amount of acetone should be increased in the order of increasing reactivity organochlorosilanes and back opposite heterogeneity area of systems: acetone-H2O-R2SiCl2: MePh2SiCl ≈ Ph2SiCl2 < Me2PhSiCl2 ≈ Me3SiCl ≈ MePhSiCl2 < Et2SiCl2 < VinMeSiCl2 < Me2SiCl2 ≈ PhSiCl3 (Fig. 1a).

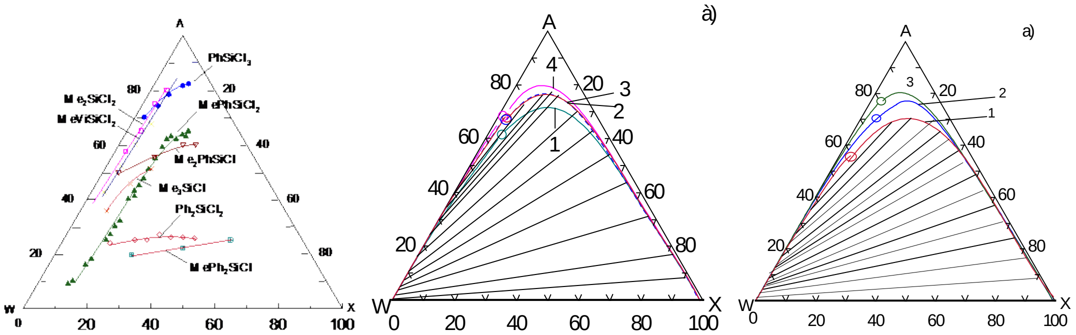

Fig. 1. Phase quasi-equilibrium diagrams of systems: acetone (A) – water (W) – X (organochlorosilane) (mol., %): a) part of phase quasi-equilibrium chords (exp.) in the water–acetone–organochlorosilane; b) Me2SiCl2 (1), MePhSiCl2 (2), PhSiCl3 (3), Ph2SiCl2 (4), and c) Me3SiCl (1), Me2PhSiCl2 (2), MePh2SiCl (3) – prediction by UNIFAC. 0 – triple (critical) point.

The reactionary RnSi(OR')4-n system as in the case of with organochlorosilane has a large immiscibility region. However, organoalkoxysilanes are lesser reactive compounds than organochlorosilanes, the rate of organoalkoxysilanes hydrolysis and the condensation are comparable. Differences between the hydrolytic polycondensation of RnSiCl4-n and RnSi(OR')4-n, are discussed in the report.

It is established that the composition of products depends on water/alkoxysilane ratio. The selection of method of synthesis (solvent free or in miscible or water-immiscible solvents (ketones, nitriles, ethers, esters, alkanes, and aromatic hydrocarbons) does not affect the composition of hydrolysis products. This fact obviously points to the kinetic regime of the process. Water delivery into the reaction zone is provided by an increase its solubility in this region due to the formation of hydrophilic molecules of organohydroxyalkoxysilanes, by alcohol homogenization, and by the fact that the diffusion of water keeps pace with the reaction. This "feeding" of reaction phase is used by LLC "SPF" MIKS" in the free-solvent technology production of silicone varnishes and resins of branched, cross array and spirocyclic structures.

Thus, we developed the theory of heterophase hydrolytic polycondensation of organosilicon monomers. It fundamentally simplify helps to the technology of the production silicones, cut the raw material and energy costs , significantly reduce pollution by replacing chlorine-containing compounds on organoalkoxysilanes and the exclusion of solvent from production.

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PRODUCING ETHYL ACETATE BY DEHYDROGENATION OF ETHANOL PROCESS MODELING

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A process of producing ethyl acetate by dehydrogenation of ethanol is considered in accordance with the following chemical reactions

$$C_2H_5OH \leftrightarrow C_2H_4O + H_2 \text{ and } C_2H_5OH + C_2H_4O \leftrightarrow C_4H_8O_2 + H_2,$$

carrying out in the presence of the NTK- 4 catalyst. The main advantage of this method over the traditional, based on the esterification reaction of ethanol with acetic acid in the presence of sulfuric acid, is that it is unnecessary to use the corrosion-resistant materials in the manufacture of basic equipment. Also advantage of this method is the use as a raw material of only one reagent – ethanol. To carry out this process has been proposed and practically implemented flowsheet, comprising two reactors (ethanol dehydrogenation reactor and reactor of the selective hydrogenation of remaining acetaldehyde to ethanol), separator and a separation unit [1]. The aim of this work is to develop and test the operation principle of technological scheme of dry ethanol dehydrogenation to ethyl acetate comprising only one dehydrogenation reactor. Exclusion from the scheme of the selective hydrogenation reactor was made possible by organizing recycling not only reagent ethanol, but also intermediate – acetaldehyde.

At the first stage of work mathematical modeling of isothermal continuous stirred tank reactor was carried out [2]. Values of the minimum volume of the reactor and recycle streams of ethanol and acetaldehyde, theoretically providing 100% conversion and selectivity of the system as a whole were found. As a result of calculation it was found that by using the isothermal reactor of perfect mixing of 4 m^3 it is theoretically possible to achieve 100% conversion and selectivity under the condition of the existence of the separation unit, which provides separation of the reaction mixture at predetermined recycle and product streams. At next step the alternative recirculating circuit, with usage of isothermal plug flow reactor instead of continuous stirred tank reactor, was considered. Calculations showed that the use of a plug flow reactor of 4 m^3 volume also allows to obtain high conversion and selectivity. It is worth to note that the usage of an isothermal plug flow reactor allowed almost three times to reduce the total required amount of the recycle stream, which in turn should lead to a decrease in energy costs. Thus, as a result of mathematical modeling of the reactor, working in recirculation system, it is shown that by using recycling of agent (ethanol) and intermediate (acetaldehyde) the process of producing ethyl acetate can be carried out in only one reactor of ethanol dehydrogenation.

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DESIGN OF NOVEL HETEROGENEOUS CATALYSTS BASED ON NANOSIZED $CoPc(SO_3Na)_4$ AND MODIFIED LAYERED ALUMINOSILICATES

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Catalysts based on cobalt tetrasulfophthalocyanine ($CoPc(SO_3Na)_4$) are the promising systems for fine purification of gases, petroleum products and liquid effluents from the sulfide impurities due to their high activity and stability to the action of the reaction medium. Heterogenization of $CoPc(SO_3Na)_4$ will allow to regulate the degree of agglomeration and permit its fixation in the most active dimeric form, and moreover, will remove secondary contamination of wastewater by cobalt. The layered clays intercalated by polymeric inorganic oxocations possess unique structural and physicochemical properties, such as high stability, large surface area, adjustable surface acidity and can be the promising materials as supports for this catalyst. The interlayer distance of the pillared interlayered clays (PILCs) (up to 1,7–2,1 nm) is comparable to the size of the molecule $CoPc(SO_3Na)_4$ (2 nm). It makes possible to intercalate molecules $CoPs(SO_3Na)_4$ in the interlayer space of PILCs without formation of a strong chemical bond.

The aim of this study is to develop the simple and manufacturable method for producing of the heterogeneous catalyst based on $CoPs(SO_3Na)_4$, which assures durable fixation of $CoPs(SO_3Na)_4$ on the support while maintaining the reactivity of the central atom of cobalt (II).

The task of this study is to investigate of the adsorption of $CoPs(SO_3Na)_4$ from aqueous solutions by layered clays of four types: Na-containing naturally occurring montmorillonite, Al-, Zr- and mixed Al,Zr-pillared montmorillonite (Na-clay, Al-PILCs, Al,Zr-PILCs, Zr-PILCs).

PILCs were prepared by the exchange reaction between Na-clay and Al-, Zr and mixed Al,Zr-cation solutions. Activity catalysts were tested in the reaction of H2S oxidation with oxygen in aqueous solution. The obtained supports and catalysts were characterized by XRD, IR and DR-UV-vis-spectroscopy, N_2 adsorption and atomic emission spectroscopy.

It was found that the quantity and nature of the adsorption depends on the nature of the cation in montmorillonite (Table). It has been shown that adsorption of $CoPc(SO_3Na)_4$ on PILC proceeds via chemical interaction between sulfonate groups and atom of metal of the fixing oxide. According to DR-UV-vis spectroscopy in the region of irreversible adsorption the degree of aggregation on the surface of Zr-CAC remains the same as that in an aqueous solution. He was adsorbed as a mixture of monomers and dimmers without formation of strong bond between central atom and support. It has been established that $CoPc(SO_3Na)_4$/Zr-PILC catalysts exhibit high activity in oxidation of sulfide solution by oxygen in a wider range of pH (7–14) and concentrations of Na2S (up to 1.3 M) in comparison with homogeneous $CoPs(SO_3Na)_4$ (pH = 7–10, C_{Na2S} – up to 0.1 M).

Physicochemical and adsorption properties of $CoPs(SO_3Na)_4$/PILCs catalysts

Sample	Al, wt.%	Zr, wt.%	S_{BET}, m^2/g	d_{001}, nm	Adsorption data	
					a_{max}, мг/г	$a_{irreversible}$, мг/г
Na-clay	5,6	0	100	14	1,2	0,0
Al-PILCs	9,8	0	200	18	4,0	~0,7
Al,Zr-PILCs	8,7	1,9	123	18,4	6,0	~0,7
Zr-PILCs	5,6	12,7	125	20,1	13,7	5,5

STUDY OF THE ADSORPTION OF THE ACTIVE SUBSTANCE CONTAINING DIPHENYLOXIDE MOIETY ON THE OUTER SURFACE OF CARBON NANOTUBES

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Closed surface structure of carbon (fullerenes and nanotubes) exhibit a number of specific properties that allow you to use them as special materials and considered as an interesting physical objects and chemical systems. A remarkable feature of carbon nanotubes (CNT) connected with their unique sorption characteristics. Strongly curved surface of the nanotube allows it to adsorb onto the surface of the organic molecules, for example, substances containing diphenyloxide moiety. These substances are new structures characterized by high levels of similarity known medicinal substances and the lack of connections marked toxic properties. They also exhibit a wide range of pharmacological properties [1]. Therefore, the combination of transport options CNT – modified biologically active molecules may lead to the creation of new nanomaterials for targeted drug delivery within living organisms [2].

The paper presents the theoretical calculations of the adsorption of the active substance – 1-(3-phenoxyphenyl)-2-cyano-ethylene on the CNT's surface. The calculations were performed using the semiempirical PM6 scheme in the software package Gaussian. PM6 scheme was chosen because of good reproduction of intermolecular interactions and geometry of atomic systems. Calculations were used to model the CNTs with chiral (2,5) and (5,5). As a result of the calculations have been optimized geometries of atomic systems and identified specific spatial configuration of molecules. Adsorbed to the active version of the nitrile was considered a single-site adhering to the surface of CNTs. The calculations made it possible to construct the potential energy surface profile for the adsorption process. Analysis of the energy curves found that the nitrile molecule is adsorbed on the CNT surface, as evidenced by the presence of a minimum on the energy curve. Potential energy values are normalized to the sum of the total energies of non-interacting systems.

Analysis of the data showed that the adsorption of the active substance – 1-(3-phenoxyphenyl)-2-cyano-ethylene and possible chiral CNT (2,5), and achiral CNT (5,5). In the first case corresponds to the physical adsorption of the interatomic distance of 3 Å and energy -0.0521 eV; Second physical adsorption corresponds to the interatomic distance 3.1 Å and energy -0.0464 eV.

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STUDYING THE PROPERTIES OF THE CATALYSTS IN HYDROTREATING OF THE PETROLEUM FRACTIONS

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The catalysts of hydrodesulfurization petroleum fractions hydrotreating processes based on the universal composition – Co(Ni)Mo(W)S, on the supporting medium, as which hitherto used almost exclusively byγ-Al_2O_3. The system is universal and capable of changing its activity and the selectivity depending on the methods and techniques synthesis, introduction of various modifying supplements, changing the conditions of sulfiding, application of various the supporting medium, the active components, etc.

In our work, we have the following results: developed a series of the Al-Mo-W-catalysts (aluminum-molybdenum-wolfram), detailed description of the physical properties and composition of the catalysts, definition of hydrodesulfurization activity of the Al-Mo-W-catalysts, estimation of these catalysts possibility to use for deep hydrodesulfurization of petroleum fractions. The series of the Al-Mo-W-catalysts have developed on supporting medium- γ-Al_2O_3. The molybdenum trioxide and tungsten trioxide deposited by impregnation the salts of $(NH_4)_2MoO_4$ and $(NH_4)_4W_5O_{17}\times2.5H_2O$ respectively. The fraction of the trioxide total mass in the catalyst was: 3% и 10%; 6% и 10%; 3% и 15% (WO_3 и MoO_3).

The hydrotreating researches have conducted on the diesel, gasoline and kerosene oil fractions (table), at temperatures of 320–360°C, at a pitch of 20ºC, at a hydrogen feed rate 6 l/h. The duration of test run 1 hour, pre-activation in the hydrogen flowing 2 hour, the fresh feed rate 15-20 ml/hr. Since sulfur compounds are the most faithful and undesirable criterion, the degree of treatment from sulfur is the main index.

The results of the hydrotreating

Type of raw material	**Original cont. of S, ppm**	**Final cont. of S, ppm**	**Degree of treatment, %**
Dieselfraction	0,90	0,10	88,9
Dieselfraction	0,87	0,12	86,2
Dieselfraction	0,83	0,10	87,0
Gas-condensate	0,68	0,09	86,8
Dieselfraction	0,67	0,12	82,1
Gas-condensate	0,38	0,10	74,7
Dieselfuel	0,16	0,05	68,8
Gasoline	0,13	0,04	69,2
Dieselfuel	0,08	0,02	75,0

In the future, the effect of MoO_3 and WO_3 content has studied on the hydrodesulfurization activity of bimetallic catalysts. Then catalysts activity had tested on the three types of fuels, that is: diesel fraction (original content of S – 0,90 ppm wt), diesel fraction (original content of S – 0,67 ppm wt) and automotive gas oil (original content of S – 0,08 ppm wt).

The graphs showed, that the catalyst 3% WO_3, 15% MoO_3/γ-Al_2O_3 has maximum degree of treatment 86.8 and 88.5% on the diesel fraction , and the final content of the sulfur-containing compounds -0,11 и0,1 ppm wt respectively.The catalyst 6% WO_3, 10% MoO_3/γ-Al_2O_3 has showed the hydrodesulfurization activity -68.8 и 74.7%, the final content of the sulfur-containing compounds – 0,05 и 0,1 respectively. The obtained results allow to compare the catalysts 3% WO_3, 15% MoO_3/γ-Al_2O_3 and 6% WO_3, 10% MoO_3/γ-Al_2O_3 with industrial DN-

200 and HR-526 ones.The gas-condensate JSC «Condensate» has used to compare the hydrodesulfurization activity of 3% WO_3, 15% MoO_3/γ-Al_2O_3 with HR-526; the original sulfur 0,68 ppm wt. The gasoline AtyraurskyOR has used for comparison the 6% WO_3, 10% MoO_3/γ-Al_2O_3 and DN-200, the initial sulfur content 0,08 ppm wt.

The results obtained for the catalysts 3% WO_3, 15% MoO_3/γ-Al_2O_3 and HR-526 has allowed to judge of a similar degree of desulfurization in the entire temperature range. The maximum degree of the catalyst hydrotreating has investigated 86.8%, whereas the HR-526 – 85.3%. Lower production cost of the test catalyst 3% WO_3, 15% MoO_3/γ-Al_2O_3 allows to consider it as a cheap but effective hydrotreating catalyst of high sulfur petroleum fractions.The data on the catalyst 6% WO_3, 10% MoO_3/γ-Al_2O_3, and DN-200 has showed that the catalyst analyzed 6% WO_3, 10% MoO_3/γ-Al_2O_3 has had higher hydrodesulfurization activity, degree of purification amounted 69.2% , at a residual content of sulfur components – 0,04 ppm wt, that meets the requirements of EN 590. Hence, it can be used for the processes of recycling and improving the quality of fuel oil.

THE EFFECTS OF LOCAL MAXIMUMS FOR AFC OF "CSTR + REACTION $A_1 \to \alpha_2 A_2 \to \alpha_3 A_3$" AT HARMONIC PERTURBATIONS OF SPEED OF STREAM

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The account of small perturbations and the calculation of local effects are one of the key problems of development of mathematical and numerical modeling.

The problem of description of a non-stationary operating mode of the continuous stirred tank reactor (CSTR) at passing of a consecutive irreversible reaction in conditions of harmonic fluctuations of volumetric speed $\bar{v} = 1 + \mathrm{E}_v \sin \bar{\omega}\tau$ of a stream is examined.

The formulas for calculating the amplitude-frequency characteristics (AFC) at relatively small perturbations E_v □ $\zeta_{i(v)}^{-1}$ has been obtained

$$\zeta_{1v} = \frac{\tilde{a}_1}{\sqrt{A_1^2 + \bar{\omega}^2}}, \; \zeta_{2v} = \sqrt{\frac{a^2 + \bar{\omega}^2}{(A_1^2 + \bar{\omega}^2)(A_2^2 + \bar{\omega}^2)}}, \qquad (1)$$

where $\zeta_{i(v)} = \mathrm{E}_{i(c)} / \mathrm{E}_v$ – is the simplex of amplitude of concentration and of amplitude of speed; $a_i = n_i \tilde{a}_i$, $A_i = 1 + a_i$ – is the transform coefficients (sensitivities) of subsystems [1–3]; $\bar{\omega} = \omega\tau_0$ – is the complex of cyclic frequency ω; τ_0 – is the mean time of stay of ingredients in CSTR; $a(\tau_0) = n_1 \tilde{a}_1 \tilde{a}_2 - 1$ – is the complex of transform coefficients. The value of $a = 0 \Leftrightarrow n_1 \tilde{a}_{1\bullet} \tilde{a}_{2\bullet} = 1$ corresponds exactly to the maximum yield of main product A_2 [1].

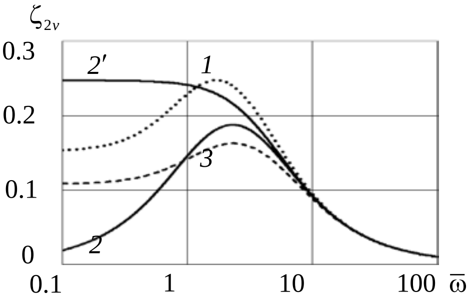

Figure. AFC of the system for reaction of first $n_i = 1$ orders at different values of degree of transformation x_0:
1 – $x_0 \approx 67\%$ $(a < 0)$, *2* – $x_{0\bullet} = 75\%$ $(a = 0)$, *3* – $x_0 = 80\%$ $(a > 0)$; *2′* – $x_0 = 75\%$ $(\mathrm{A}_1 \to \alpha_2 \mathrm{A}_2)$.

As follows from the figure, for AFC of the system there are local maximums on frequency. The points of the maximums $(\partial\zeta_{2v} / \partial\bar{\omega} = 0)$ are equal

$$\bar{\omega}_{\mathrm{m}}^2 = \sqrt{(A_1^2 - a^2)(A_2^2 - a^2)} - a^2, \; \bar{\omega}_{\mathrm{m}}(a = 0) = \sqrt{A_{1\bullet} A_{2\bullet}} \overset{[n_i = 1]}{=} (x_{0\bullet} c_{0\bullet})^{-1/2}, \qquad (2)$$

where $x_{0\bullet} = 1 - c_{0\bullet}$ – the degree of transformation of reagent A_1 in point of the maximum.

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PHYSICO-CHEMICAL PRINCIPLES OF LIQUID-PHASE ALCOHOLS HYDROCHLORINATION

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The hydrochlorination of primary alcohols is known to be a bimolecular nucleophilic substitution reaction. The reaction rate equation is

$$w = k_0 \mathrm{e}^{-\frac{E}{RT}} C_{\mathrm{ROH}} C_{\mathrm{HCl}}$$

However, it is noted in many works on the hydrohalogenation of alcohols that the concentration of water has an effect on the reaction rate. Even a small amount of water decreases the reaction rate noticeably. The mechanism of the influence of water on the rate of the hydrochlorination of alcohols has not been established yet.

Our experiments [1, 2] by hydrochlorination of polyhydric alcohols have also shown that the water affects the reaction rate. This is explained by the high solvating power of water. The chloride anions, which have a significantly smaller size than organic molecules and bear a whole charge undergo preferential solvation. The smaller the size of a molecule being hydrated and the higher its polarity, the stronger its bond with the hydration shell, i.e., in other words, the higher the energy of hydration. It is because of the formation of hydration shells that it is necessary to consider the solvent as an agent participating directly in the reaction. The higher the concentration of water in the reaction mixture, the larger the number of its molecules that interact with the chloride anion and the stronger the hydration shell of the latter, and, consequently, the higher the energy of activation and the lower the rate of the reaction. Therefore, to describe the rate processes hydrochlorination alcohols in the kinetic equation was introduced coefficient γ. This coefficient describes the degree of hydration and the anion is a chlorine concentration ratio of water to the hydrogen chloride concentration.

This method has been studied hydrochlorination reaction such simple monohydric alcohols such as methanol and ethanol. The kinetics of the liquid-phase hydrochlorination of methanol was studied at 40-65°C and water concentrations of 0.5 to 13 mol/l, so the coefficient γ varied from 0.5 to 1.5. Results possible to determine the equation of the rate of formation of methyl chloride.

$$w_{\mathrm{CH_3Cl}} = 1.89 \cdot 10^{10} \cdot \gamma^{1.38} \cdot e^{-\frac{101850 + 4800 \cdot \ln\gamma \pm 100}{RT}} \cdot C_{\mathrm{CH_3OH}} \cdot C_{\mathrm{HCl}}\ ,\ [\mathrm{mol \cdot l^{-1} \cdot s^{-1}}]$$

The kinetics of the liquid-phase hydrochlorination of ethanol was studied at 60-80°C and water concentrations of 2.1 to 13.4 mol/l, so the coefficient γ varied from 0.3 to 2.0. The equation of the rate of formation of ethyl chloride is

$$w_{\mathrm{C_2H_5Cl}} = 5.70 \cdot 10^{3} \cdot \gamma^{1.76} \cdot e^{-\frac{63800 + 6120 \cdot \ln\gamma \pm 100}{RT}} \cdot C_{\mathrm{C_2H_5OH}} \cdot C_{\mathrm{HCl}}\ ,\ [\mathrm{mol \cdot l^{-1} \cdot s^{-1}}]$$

The resulting kinetic equations are empirical and are valid in the studied ranges of temperature and reagent concentrations. Thus, these studies support the hypothesis that the solvation effect has a significant impact on the rate of liquid phase Hydrochlorination all alcohols.

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DINAMICS OF THE PHASE QUASI-EQUILIBRIUM IN HYDROLYSIS OF ORGANOCHLOROSILANES AND ORGANOALKOXYSILANES

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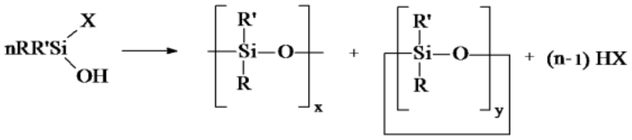
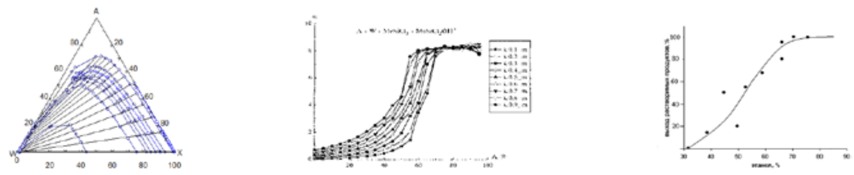
Previously, it has been found that hydrolysis of R_nSiX_{4-n} (X = Cl, OR; n = 1 ÷ 4) is a combined heterophase reactive mass-transfer process (reaction 1).[1, 2]

$$R_2SiX_2+H_2O \rightarrow R_2SiX(OH) \quad (1)$$



$$nRR'Si(X)(OH) \longrightarrow \left[-Si(R')(R)-O-\right]_x + \boxed{\left[-Si(R')(R)-O-\right]_y} + (n-1)\,HX \quad (2)$$

Polyorganosiloxanes are produced in the organic phase of the reaction system by the heterofunctional condensation of hydrolysis products (reaction 2)[1]. Charge rating m = $[H_2O]/[R_nSiX_{4-n}]$ in the reaction phase to define the molecular weight and structure of the polymer, while m set indirectly by total mass mixing ratio. Formation $R_nSiX_{3-n}(OH)$ leads to an increase of the homogeneous area. Because the reaction system moves to the formation of products, so it passes through the many of intermediate quasi-equilibrium states. Heterophase water-acetone-R_nSiCl_{4-n} (n = 1÷4) systems are calculated on the basis of group models by UNIFAC. Figure 1a snows the changing phase separation during the transition from the initial reaction system to intermediate water-acetone-$MeSiCl_3$-$MeSiCl(OH)_2$ by step 0.1 $MeSiCl_2OH$. According to the phase equilibrium calculation, we obtained series the amount of acetone in the system – ratio water/methyltrichlorosilane in the organic phase relationships for different amounts of $MeSiCl_2OH$, which formed in the hydrolysis pathway. (Fig.1b). In contrast with RnSiCl4-n reaction systems, phase equilibrium of the water-acetone-$R_nSi(OR')_{n-1}$ (n = 1÷4) is determined experimentally and by equation NRTL. It looks similar. The geterogeneous area in such systems is slightly smaller than in organochlorosilanes systems. In addition, the resulting $RSi(OR')_2OH$ and alcohol reduces the geterogeneous area. The concentration of water rises in the reaction (organic) phase, causing yield of soluble polymer increase (Fig. 1c).



a b c

Fig. 1. a) Diagram of phase equilibrium water-(W)-acetone-(A)-X, X: $MeSiCl_3$ + $MeSiCl_2(OH)$; b) Dependences of the calculated m = $[H_2O]$ / $[MeSiCl_3]$ ratio in the organic phase of the reaction vs the amount of solvent (mass fraction); c) Dependence of the soluble polymer vs the amount of solvent (mass fraction).

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PURIFICATION OF NATURAL QUARTZ UP TO HIGH LEVEL

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Novel method of purification granulated quartz was originated and tested in terms of Guberlinka deposit. Production of high purity quartz powders may be considered as protracted problem of high-tech technologies. Researches in field of natural quartz purification usually are carrying on minimal laboratory samples thus all methodologies concerning optimization of reagent type, procedure conditions (temperature, time, concentration) in fact were no good.

We took into consideration one interesting study (Kotova E.N and joint authors) conducted in 2010 which showed that hydrochloric acid vapors better etch quartz surface than HF with analogical concentration. Majority of microimpurities in quartz after 26% HCl treatment at 1000°C were absent. Alternative methods consists in chlorination with Cl_2 at 1200°C (3 l/g SiO_2) or other agents and were of no interest. However the mechanism of acid chlorination with diluted HCl was in need of an explanation as long as any adequate versions hitherto were absent. Simple alternative consists in volatile chloride formation was of no worth.

For the purpose of practical task implementation we executed the large-scale pilot project with lump minerals from Guberlinka deposit. Powerful electric impulses (impulse voltage generator) in deionized water flow along discharge channels on grain boundaries provided with required disintegration of quartz particles. Electric disintegration facilitated the realization of following chemical stages. Always before high temperature treatment granulated quartz was etched with mixed acids (HCl + HF, HCl + HNO_3 (aqua regia) at al. that hinders following regeneration of individual acids.

Our method consists of two steps. Firstly granulated 100–300 μm quartz (25–28 kg) was loaded into 50 l barrels and each portion was mixed with 4 l concentrated HF (S:L = 5:1) for 5 minutes by rotary agitation. Then batch in barrels was kept at evaluated temperature (75°C) during 6-8 h. After cleaning (conductivity of rinsewaters 1-3μS) dried (only to flowability) quartz was transferred into quartz vessels (120x2000 mm) and heated to 700–1000°C with periodic dropwise HCl feed (50 ml/1 kg quartz). Intriguing wave-like autoagitation took place. The chlorination lasted 6-8 h (day or night). The purification was attributed to “steamsolutions”. We got the excellent result: 1700 kg of fine-grained quartz powder of sort Iota-4 – Iota-6 (table) and made crucibles with diameter 45 cm from our purified quartz.

The results of chemical refining of natural quartz

Chemical element	Content, ppm					
	Before chemical treatment	After HF (75°C) (first step)	After dropwise hydrochlorination (700–1000°C) (second step)	IOTA-std	IOTA-4	IOTA-6
Na	5.1	2.9	0.36-0.11	0.9	0.9	0.08
K	3.1	0.8	0.33-0.14	0.60	0.35	0.07
Ca	21	0.2	0.20-0.17	0.5	0.6	0.6
Fe	8.8	0.2	0.15-0.10	0.28	0.30	0.15
Al	16	4.5	4.5-4.3	16.2	8.0	8.0

THE PROCESSING OF MONAZITE WITH AMMONIUM DIFLUORIDE

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Ammonium bifluoride possesses strong fluorination properties comparable with hydrofluoride acid but more user-friendly and earth-friendly. High reactivity NH_4HF_2 attributed to complexation ability of difluoride-ion HF_2^- and low reaction temperatures (not above 200°C). This fluorinating agent effortlessly recovers. Nevertheless fluorammonium treatment of monazite data was absent. This study is first attempt in this direction.

Rare earth metals in monazite ores are presented in the phosphate forms. REE ores are generally ferric, for example Russian Chuktukon deposit (50%) and others. Thus theoretically magnetic separation was possible. However result was negative. Usually magnetite forms from batch (monazite + coal) heated at 550°C for 1 h. Electronic, optical and X-ray diffraction studies reveal exclusive intergrown Fe and REE [1].

We reduce Fe_2O_3 to Fe_3O_4 with CO generated from HCOOH in sulfuric acid. Our pre-investigation showed facilitated magnetization of monazite but worst REE separation from magnetite (54.1/45.9%). We decided to perform CO reduction in moderate conditions: process was carried on at 350°C for 15 min. CO was mixed with nitrogen (1:4).

For the purpose of rupture interdependence of ferric oxide with rare earth metals we performed the fluorination of magnetized monazite with little amount of NH_4HF_2 because of Fe_3O_4 not reacted with it. REE, alumina, calx and other mineral compounds of monazite concentrate were fluorinated at 195°C within 4 h. Success of next stages depends on optimal mode of magnetization (generally reduce CO procedure duration at above mentioned conditions). Magnetic separation after fluorination allowed us extracting of 88% of cerium, 78-79% each of lanthanum, praseodymium and neodymium and samarium into nonmagnetic fraction.

REE with NH_4HF_2 formed complex salts NH_4REEF_4 are insoluble in cold and hot water, but enough well dissolve in mineral acids. The dissolution of complex fluorides was performed in hydrochloric acid (18–30%) with backflow condenser. The extraction of REE in 18% HCl corresponded to 62–64%, in 30% HCl – 80–84%. Evidently the increase of acid concentration scaled up the extraction degree. The best results (97.84%) were received for previously decomposed complex fluorides (removal ammonia fluoride, $NH_4REEF_4 \rightarrow REEF_3$) under following conditions: boiling 36% HCl, backflow condenser, time 5 h.

The annealing stage was needed for recycling of fluorinating agent. We carried on the annealing nonmagnetic fraction at 450–500°C in the open air. Mass loss (NH_4F) equals to 20% owing to the presence of NH_4FeF_4. Insoluble nonvolatile trifluorides of lanthanide elements were converted to soluble chlorides. It was interesting that preliminary removal NH_4FeF_4 from assembly of complex fluorides with diluted HCl led to lowering of chloride yield down 16%. This result was attributed to positive role of iron in procedure dissolution $REEF_{3,}$ especially after thermal dissociation of NH_4FeF_4. After distillation of azeotropic solution (18–22% HCl) we received reddish-brown acid saturated solution fitted for individual REE extraction.

To our mind proposed technology basic principles answer to ecological requirements.

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ANALYSIS OF ENERGY CONSUMPTION OF RECIRCULATION SYSTEM IN THE CASE OF CONSECUTIVE REVERSIBLE REACTIONS

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It is widely known that recirculating unreacted reagents and by-products can be used to intensify complex chemical reactions [1, 2]. The efficient separation of the primary products from the reacting mixture and subsequently returning the resulting mixture to the reaction zone allows the system to achieve 100% conversion and selectivity. However, in practice such efficient separations are not always attainable. This results in the presence of primary products in the recycle stream which in turn adversely affects the rate of the primary reaction. This work approaches this problem by investigating the effect of the recycle value and composition on the possible stationary states of the recirculation system and their corresponding energy consumption in the case of the reaction type $A \leftrightarrow B \leftrightarrow C$ [3].

By breaking down the recirculation system into its component parts, analytical expressions are derived for the system, which regardless of the method of separation employed allows accurate calculations to be made for both process verification and design purposes.

It is shown that stationary states for the recirculation system with the same values for conversion and selectivity can be obtained with different sets of values for the recycle stream S and its composition $\mathbf{x}$. The inefficient separation in the system is compensated for by increasing the recycle stream value. In the case where fractional distillation is the separation method employed, increasing the recycle stream requires an increase in the energy used by the distillation column. On the other hand, increasing the recycle stream lends the possibility of relaxing the separation efficiency requirement, i.e. the presence of otherwise unwanted components of the reaction in the recycle stream can be tolerated. This reduces the energy consumed by the column which otherwise would have been required to ensure a high separation efficiency, by reducing the column’s reflux.

Using numerical simulation it is shown that the nature of the relationship between the energy consumption and the recycle values necessary to achieve the required conversion and selectivity, using fractional distillation for the separation, is extreme. The recycle value for a specific recirculation system with given design and regime parameters allowing the attainment of required conversion and selectivity while keeping energy consumption at a minimum is found. This method is general and can be applied to the optimization of recirculation systems using the minimum cost approach.

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THEORY AND PRACTICE OF ALKYLPHENOLS PRODUCTION

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A lot of alkylphenols (AP) are industrially important compounds of large-tonnage processes of organic synthesis. Manufacturing processes of producing of spatial-hindered, partially screened and unscreened phenols are various.

At this moment it is found the following:

- Thermodynamic stability of AP increases in the ranks:

  `` spatial-screened AP << partially screened AP << unscreened AP

  ``2,6-di-*tert*-AP << 2-*tert*,6-*sec*-diAP < 2-*tert*,6-*prim*-diAP<2,6-di-*sec*-AP

  ``2-*tert*-AP << 2-*sec*-AP < 2-*prim*-AP

  ``4-AP<3-AP; 2,4-diAP≈ 2,5-diAP<3,5-diAP.
- The ranks of thermal stability and thermodynamic stability of AP coincide on qualitative level.
- Maximal equilibrium concentrations of mono-*tert*-AP and di-*tert*-AP reach 80% mol, while mono-*sec*-AP and di-*sec*-AP don’t exceed 65% mol.
- Liquid-phase mutual conversion of *tert*-(C_4,C_8)AP are carried out till equilibrium in the presence of high-activity mineral and immobilized acids. The industrial process of producing of 4-*tert*-AP is performed with exhaustive alkylation of phenol with isobutylene and practically reaching of equilibrium in the system Phenol+mono-*tert*-AP+di-*tert*-AP. Isomerization of tert-(C_8)AP is accompanied with alkyl substituent destruction, *tert*-(C_4)AP generate in the ratios closed to equilibrium.
- Products of oligomerization of branched (C_4,C_8)alkenes and alkylation of phenol with them are found out in the reaction mass even at large phenol excess in the initial mixture. This makes considerable problems in the organization of recycling in continuous processes of target AP producing.
- Alkylation of phenol with isopentene with *tert*-(C_5)AP generating accompanies with isomerization of carbon structure in AP. Secondary structures prevail over tertiary ones in the equilibrium.
- Liquid-phase alkylation of phenol with higher linear alkenes gives *orto*-*sec*-AP and *para*-*sec*-AP in the ratios closed to static quantity. “O*rto*-*para*” isomerization practically doesn’t course on high-activity immobilized acids, secondary alkylphenol ethers converse in AP quantitatively, isomerization of alkenes compete with alkylation reaction.
- The presence of moisture in the system decrease significantly the activity of all immobilized acids.
- Critical temperatures of layering in the system Phenol+Alkene+Water depend on content of moisture significantly, which sources are variable in continuous domestic processes.

These and other issues will be considered on conference.

This work was financially supported by the Ministry of Education and Science of the Russian Federation within the framework of the basic part of governmental tasks of Samara State Technical University (project code 1708).

USING HEAT PUMPS IN ASSOCIATED AND COMBINED MASS TRANSFER PROCESSES

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Use of combined and associated mass transfer processes for separation and purification of substances from impurities significantly expands the range of possible separation. However, such processes are often associated with significant energy costs. At the same time, we know that different heat pumps began to be widely used in recent years in order to reduce energy costs of a series of processes. Given this, we performed an analysis of different combined processes of separation and purification of substances from impurities using a vapor compression pumps.

So a combined evaporation crystallization process used for removing dissolved matter from aqueous solutions and solvent recovery from the mother liquors discharged when recrystallization cleaning substances from the impurities was investigated. At such a separation as an open-type heat pump, which was carried out compression secondary vapor and close-type pumps closed loop circulation of intermediate coolant can be used. The effect of various process parameters on the energy efficiency of the process was found.

A number of related mass transfer processes in relation to the purification and separation of organic and inorganic substances was also investigated. Heat released an the crystallization stage can be used in the implementation process of purification of substances by their recrystallization using heat pumps, can be used for heating solutions on the dissolution step. In this case, heat pump gated closed loop was applied for the temperature potential changing.

Close-type heat pump was also applied in the separation of organic mixtures by fractional melting. In this case heat generated in the crystallization step was used for heating the mixture to be separated at the stage of partial melting. Studies of the process of separation of binary mixtures by combining the processes of continuous distillation and fractional crystallization using open and close-types heat pumps were also carried out.

Specific heat costs was used to assess the energy efficiency of these processes using energy conversion efficiency and costs of conditional fuel to conduct the considered processes. Studies have shown that the use of heat pumps during combined and associated mass transfer processes allows a 30-40% reduction in the cost of thermal energy compared to conventional separation.

THEORETICAL FOUNDATIONS OF DECARBOXYLATION PROCESS OF C_{18} FATTY ACIDS – PROSPECTIVE SECOND-GENERATION BIOFUEL

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Second generation biofuels traditionally include all fuels which are received through various high-temperature methods for processing of biomass such as cellulose, lignin and other chemical components contained in wood or fiber biomass. This is mostly fast pyrolysis with the formation of solid biomass liquid hydrocarbons. With this technology, the efficiency of energy production from vegetable feeds is approximately 40-50%, and weight of liquid fuels is not more than 20-30% from the initial feed.

The way out from this situation is presented in the current work. To do this, instead of various kinds of wood feed, it is recommended to use already received high tonnage product of its processing, which is produced at almost all pulp-and-paper mills of Russia. This is tall oil. It is a byproduct wood processing, produced in the quantities of 2–3 million tons per year. It contains fat, resin and unsaponifiables, which are potential hydrocarbons for production of diesel fuel. The only drawback is that tall oil at 80–90% consists of monocarboxylic acids ($R_{(17\text{-}19)}$–COOH), unlike paraffins of crude oil. So, unlike the traditional way of producing biofuels – method of esterification of low-molecular alcohol with fatty acids resulting in production of complex esters – biodiesel, in the present work it is proposed to carry out the process by direct transfer of monocarboxylic acids of tall oil to paraffin hydrocarbons using processes of decarboxylation or decarbonation of fat and resin acids contained in it.

In laboratory conditions it has been tested the periodic process of thermal catalytic conversion of fatty (C_{18}) and resin acids (C_{20}) of tall oil to the appropriate paraffin and other hydrocarbons to find the most suitable conditions for carrying out the reactions of decarboxylation and decarbonation.

It has been established, that the progress of decarboxylation can be monitored by reduction of acid number and saponification number, which is responsible for the presence or absence of carboxyl group. The process was studied in the liquid phase in the temperature range from 240 to 320ºC with increments of 20ºC in the presence of nickel catalyst on the carrier.

It has been established that at temperature from 280 to 300^{o}C in the reaction products it was observed an increase in concentration of paraffin and olefin hydrocarbons (monocarboxylic acids in tall oil are predominantly of olefinic and diene structure) more than 50–60% by weight.

THE STUDY OF CONJUGATED CARBONYLATION PROCESSES OF UNSATURATED COMPOUNDS BY ELECTRON AND INFRARED SPECTROSCOPY

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Catalytic reactions are the basis of many chemical industrial processes. The information about the detailed mechanism of a process and about the distribution of metal complexes *in situ* is necessary to design and to improve catalysts and catalytic systems. It is very important for the catalyst design for coupled reactions on the basis of the kinetic coupling principle [1]. The palladium-containing homogeneous catalytic systems are used to obtain valuable organic synthesis products: carboxylic acids and their derivatives [2].

The reaction (1) is coupled with the reaction (2) in the $PdBr_2$–$CuBr_2$–THF–H_2O catalytic system (30°C and atmospheric pressure):

$$CO + 0.5\ O_2 = CO_2 \qquad (1)$$

$$RCH{=}CH_2 + CO + H_2O = RCH(COOH)CH_3 + RCH_2CH_2COOH \qquad (2)$$

The carbonylation of acetylene yields succinic and maleic anhydrides in the $PdBr_2$ – LiBr – AN catalytic system (3).

$$C_2H_2 + 2CO + H_2O \rightarrow \text{succinic anhydride} + \text{maleic anhydride} \qquad (3)$$

This study deals with the mechanism of these conjugated processes. The aim of this research is to study the state and the equilibrium of palladium and copper complexes in above-mentioned catalytic solutions. The information on the complexation in these systems is essential for the discrimination of hypotheses about the mechanism of catalytic reactions (1-3). The model solutions containing components of catalytic systems in various combinations, as well as the catalytic solutions during the conjugated processes were studied by electron and infrared spectroscopy. The assignment of the absorption bands to different palladium and copper complexes has been carried out.

It was shown that the copper(I) complexes were formed as result of the reduction of copper(II) complexes by carbon monoxide when the $CuBr_2$ – THF – H_2O system was purged by CO.

The state of complexes in $PdBr_2$ - LiBr – THF and $PdBr_2$ - LiBr – AN systems has been studied after purging by carbon monoxide. It has been shown that the palladium(II) carbonyl complexes dominate in $PdBr_2$ - LiBr – THF system under carbon monoxide atmosphere (the band at 2104 cm^{-1}) and the palladium(II) carbonyl complexes (the band at 2120 cm^{-1}) and the palladium(I) carbonyl complexes (the band at 1908 cm^{-1}) present in acetonitrile system.

During the coupled process of carbon monoxide oxidation and alkene hydrocarboxylation (1, 2), copper exists in the form of copper(I) compounds, and palladium is present in the form of palladium(II) carbonyl complex and probably in the form of the complex with the corresponding alkene. In the course of the acetylene carbonylation palladium is probably present in the form of palladium(I) complexes with carbon monoxide and maleic anhydride.

This investigation was supported by RFBR, grant №14-03-00052.

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QUANTUM CHEMICAL STUDY OF THE ELECTRON STRUCTURE OF DITHIOLS, THIOLS AND THEIR RADICALS

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Development of different directions in organic synthesis of biologically active substances, medicines and other materials requires extensive use of mathematical modeling methods, allowing to perform a structural analysis of the initial, intermediate and final products. Organic sulfur compounds, such as dithiols, thiols and their radicals are involved in a large number of processes in the different phases and it determines the properties of the final stage.

We are working to expand the scale of electronegativities $\chi(R)$ with the inclusion of functional groups containing polyvalent atoms of sulfur and oxygen. At this stage the aim was to obtain $\chi(R)$ groups forming $HS\text{-}(C_nH_{2n})_n\text{-}SH$, $n\text{-}C_nH_{2n+1}\text{-}CSH_3$ and $n\text{-}C_nH_{2n+1}\text{-}(CS)^{\bullet}H_2$, where $1 \leq n \leq 9$. The distributions of the electron density $\rho(r)$ of all structural conformers were studied and the characteristics of their constituent fragments by the "quantum theory of atoms in molecules" (QTAIM) [1] were found using AIMALL [2]. The geometry of the ground state of the investigated structures was determined with program GAUSSIAN 03 [3] by the B3LYP/6-311 + + G (3df, 3pd) method.

Quantum-chemical study revealed transferable parameters for the functional groups in the compounds (see Table). So SH group in the $HS\text{-}(C_nH_{2n})_n\text{-}SH$ and $C_nH_{2n+1}\text{-}SH$ has the same electronic properties. In the isomers of radicals $n\text{-}C_nH_{2n+1}\text{-}CH{=}S^{IV}H^{\bullet}$ and $n\text{-}C_nH_{2n+1}\text{-}C^{\bullet}{=}S^{IV}H_2$ the equal value of spin density localization ($\sigma(R)$) was noted in groups containing multiple bonds $\sigma(CH{=}S^{IV}H^{\bullet}) = \sigma(C^{\bullet}{=}S^{IV}H_2) = 0{,}92$ with the most concentration on the carbon atom.

Parameters of transferable groups R, charge q(R) in a.e., total electronic energy E(R) in Hartree, volume V(R) in cm^3/mol, spin density $\sigma(R)$, for $HS\text{-}(C_nH_{2n})_n\text{-}SH$, $n\text{-}C_nH_{2n+1}\text{-}CSH_3$ and $n\text{-}C_nH_{2n+1}\text{-}(CS)^{\bullet}H_2$ compounds

	CH_3	CH_2	$S^{II}H$	$CH{=}S^{IV}H_2$	$CH{=}S^{IV}H^{\bullet}$	$S^{IV}H^{\bullet}$	$C^{\bullet}{=}S^{IV}H_2$	$S^{IV}H_2$
***q*(*R*)**	-0.015	0.000	-0.060	-0.040	-0.091	0.090	-0.056	0.282
***E*(*R*)**	-39.844	-39.244	-	-438.851	-438.320	-399.670	-438.201	-400.206
***V*(*R*)**	19.9	14.1	23.8	37.5	35.6	23.1	36.4	24.2
σ(*R*)	-	-	-	-	0.93	0.21	0.92	0.17

The united qualitative scale $\chi(R)$ for the compounds $HS\text{-}(C_nH_{2n})_n\text{-}SH$, $n\text{-}C_nH_{2n+1}\text{-}CSH_3$ and $n\text{-}C_nH_{2n+1}\text{-}(CS)^{\bullet}H_2$ is represented by the inequality:

$$\chi(\mathbf{S^{IV}H_2}) < \chi(\mathbf{S^{IV}H^{\bullet}}) < \chi(\mathbf{CH_2}) < \chi(\mathbf{CH_3}) < \chi(\mathbf{CH{=}S^{IV}H_2}) < \chi(\mathbf{C^{\bullet}{=}S^{IV}H_2}) < \chi(\mathbf{S^{II}H}) < \\ < \chi(\mathbf{CH{=}S^{IV}H^{\bullet}})$$

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UNCONVENTIONAL SELECTIVE SUBSTANCES FOR AZEOTROPIC MIXTURES SEPARATION

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Extractive distillation (ED) is one of the most common methods to separate azeotropic mixtures, which are impossible for separation by ordinary distillation. The ED consequence is largely determined by the choice of a suitable entrainer. In a chemical production, distillation columns consequences and their support facilities can have a strong impact on the total capital cost (up to one-third) and on the energy consumption (up to half). That is why the design and optimization of the ED processes and recovery columns is critically important for the economics of the entire production.

Traditionally heavy boiling entrainers are used for ED separation, the solvent screening process is usually based on the empirical and half-empirical guidelines. The last decades the new processes (distillation with middle or light boiling entrainers, binary entrainers) and new solvents (ionic liquids (ILs), branched polymers, deep eutectic solvents) were intensively investigated.

Ionic liquids have become a subject of most intensive studies. Negligible vapor pressure, wide liquid range and stability at high temperatures – that is what makes them good replacements for conventional entrainers. An incredible amount of works are being published on the properties of pure ILs as well as on the measurements of activity coefficients at infinite dilution of organic solvents in ILs, which is an important and useful tool for separation problems. Also for the ED process design rigorous, robust and reliable thermodynamic models are crucial. The success of this step depends on the availability of the parameters for the chosen models and the development of thermodynamic models for electrolyte solutions.

Hyperbranched polymers and supercritical fluids are also possible for separation needs, the process of collecting VLE data is going on. Deep eutectic solvents were firstly proposed for extraction, the further investigations are required.

This work represents the analysis of possibilities of using unconventional solvents and their comparison with traditional solvents for extractive distillation of binary azeotropic mixtures based on the data published in Elsevier, Springerlink, Wiley, ACS and other international publishing houses from 2004 till nowadays.

COMPARATIVE ANALYSIS OF DEHYDRATION VARIANTS OF ETHYL ALCOHOL BY VARIOUS SUBSTANCES FORMING HETEROAZEOTROPE

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Currently, ethanol is widely used as an additive to fuels (gasoline brands E5 and E10), what require obtaining the product containing not less than of 99.97 vol.% of key component. Dehydration of products in the technology of organic substances is often carried out by heteroazeotropic distillation. The essence of this method is to add to the mixture specially selected entrainer (E), which have to form an new azeotrope with one (or more) component of the initial mixture, as well as to have with him limited solubility, which facilitates agent regeneration.

The present work is devoted to a comparison of dehydration variants for separating ethanol – water mixture of azeotropic composition using substances of different classes of organic compounds which form heteroazeotrope, e. g. hexane, cyclohexane, benzene. Structure of the phase diagrams of ternary systems studied ethanol (1) – water (2) – E (3) contains three binary saddle azeotrope and ternary node azeotrope with a minimum boiling point. Binary azeotrope water – E and ternary azeotrope is located in a two-phase delamination region of closed type. Analysis of balance ratios in the different time-space contours of scheme are produced by the balance simplexes method. Directed graph is shown at the Figure (Rij – flow stream from unit i to unit j; D – decanter). To calculate the entire flowsheet the amount of all streams assuming columns with infinite separation capacity is determined. Results given in the table show that the main influence on the amount of recycle streams comes from the composition ternary azeotrope, the ratio of equilibrium liquid phases, the position liquid-liquid tie lines (distribution coefficient of ethanol between aqueous and organic phases).

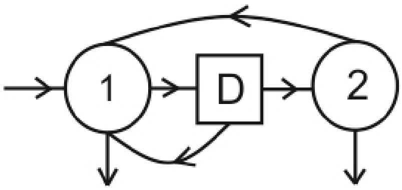

Fig. Directed graph of complex heteroazeotropic distillation

The influence of various factors on the total flow of recycle stream

Separation agent	$X_E^{tern.az.}$, mol.fr.	Flow of recycle stream, kmol/hr		Ratio R_{D1} / R_{D2}
		R_{21}	R_{d1}	
hexane	0,6331	41,57	107,85	1,96
cyclohexane	0,5270	38,96	61,35	1,18
benzene	0,5276	22,39	44,71	1,27

Mathematical modeling of vapor-liquid phase equilibria of investigated ternary systems and liquid-liquid equilibria is produced by AspenPlus 7.3 software. Static parameters of the separation units and the total energy consumptions of flowsheets which correlated with the magnitude of the total recycle flow, are defined.

KINETIC ASPECTS OF *p*-TOLUENESULPHONIC ACID EFFECT ON Pd-CATALYSED HYDROCARBOMETHOXYLATION OF CYCLOHEXENE

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Carbonylation of olefins catalysed by transition metal complexes is a promising process for the manufacture of various organic compounds, including pharmacological and agrochemical agents [1]. An important carbonylation process is alkene hydrocarbalkoxylation catalysed by palladium complexes, which represents a one-step route from accessible alkenes to diverse esters. This process has found use in industry [2]. However alkenes hydrocarbalkoxylation catalysed by palladium catalytic systems is a very complicated process, some reactants and catalytic system components influence on the reaction rate. In this work as this reaction, we chose hydrocarbomethoxylation of cyclohexene, as all of its reaction sites are chemically equivalent, and methyl cyclohexanecarboxylate is formed as the only hydrocarbomethoxylation product. In addition, for cyclohexene we did not expect a noticeable copolymerization with CO. $Pd(PPh_3)_2Cl_2$ / PPh_3 / p-toluenesulphonic acid (TsOH) system was chosen as catalyst of the cyclohexene hydrocarbomethoxylation. The hydrocarbomethoxylation of cyclohexene was studied in the batch reactor. The experiments were carried out in toluene at constant temperature and CO pressure ($2.1 \cdot 10^6$ Pa). During kinetic experiments, the reaction mixture was sampled at particular time intervals, and the samples were analyzed by gas liquid chromatography with a flame ionization detector.

The kinetic regularities of p-toluenesulfonic acid and water effects on the cyclohexene hydrocarbomethoxylation rate have been studied. S-formating dependences of the initial rate on the $TsOH \cdot H_2O$ concentration in the 368-388 K range and the extreme dependences on the water concentration at 378 K have been received. The received data were interpreted by the hydrocarbalcoxylation hydride mechanism. In single-factor experiments at variety of TsOH concentration the effective constants of the kinetic equation

$$r = \frac{k C_{\mathrm{Pd}} P_{\mathrm{CO}} [\mathrm{cyclohexene}]\,[\mathrm{TsOH}]^2 [\mathrm{CH_3OH}]}{\left\{1 + a \cdot [\mathrm{CH_3OH}]^2 + b \cdot P_{\mathrm{CO}}^2 + c \frac{P_{\mathrm{CO}}}{[\mathrm{PPh_3}]} + d \frac{[\mathrm{CH_3OH}]}{[\mathrm{PPh_3}]} + e \cdot [\mathrm{PPh_3}]^2 + f \cdot \mathrm{C_{Pd}} + g \frac{[\mathrm{TsOH}]^2}{[\mathrm{PPh_3}]}\right\}}$$

and the effective activation energies has been estimated. The less stability of $Pd(PPh_3)_2(H_2O)_2$ complexes in comparison with $Pd(PPh_3)_2(CH_3OH)_2$ was established.

The reported study was partially supported by RFBR, research project No. 14-08-00535.

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REACTIVITY OF C_5-, C_6-EPOXYCYCLOALKANES IN THEIR REARRANGEMENT ON LITHIUM PHOSPHATE

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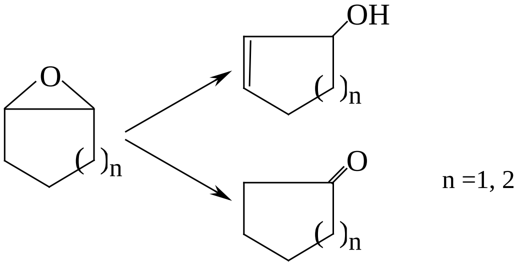
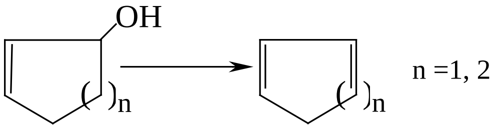
The isomerization of epoxycyclopentane and epoxicyclohexane on several samples of lithium phosphate supported catalysts was studied in a vapor phase.



The influence of temperature on the rearrangement of epoxides was studied in a flow reactor at the temperatures of 175–285 °C and volume rates of feed 0.5–3.6 h^{-1}. The optimum values of temperature and the rate of feed were chosen for each sample.

The rearrangement proceeds mainly to the corresponding cycloalkenols and cycloalkanons. Unsaturated alcohols with increasing temperature are more and more dehydrated to dienes.



The epoxicyclohexane was shown to be more active in reaction of isomerization than epoxycyclopentane and the formation of unsaturated alcohol from it prevails over the rearrangement to ketone. The isomerization of epoxycyclohexane partially proceeds with narrowing of cycle to cyclopentylcarbaldehyde.

Increase of temperature causes to reduction in the yield of unsaturated alcohols. The reason for this is not only the dehydration of alcohol, but its participation in the reaction of isomerization, etc. So, the presence of cyclohexenone, cyclopentenone and cycloalkanols in isomerizate is associated with redox reactions between unsaturated alcohols and carbonyl compounds. Similar transformations are earlier marked at the rearrangement of epoxyalkans on lithium phosphate.

The kinetics of C_5-, C_6-epoxides rearrangement was studied at temperatures of 255–285°C. The reaction was well described by the kinetic equation of the first order. The rate constants and the activation energy of the reaction were determined. Their values equal to 25.7 and 30.7 (kcal / mol) for epoxycyclopentane and epoxycyclohexane respectively.

At a temperature of 275°C the rate constants of epoxides rearrangement for cyclohexene, cyclopentene, and hexene-1 had a ratio of 1: 0,4: 0,3 respectively.

SOME FEATURES OF CONDENSATION OF CYCLOPENTADIENE WITH TRIACETONEAMINE

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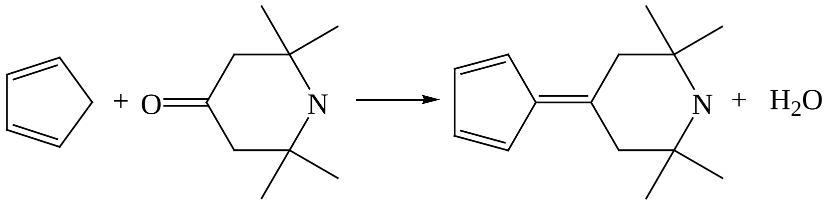
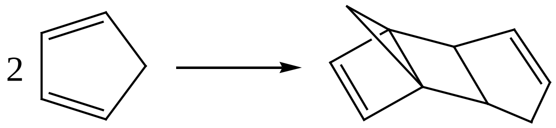
The synthesis of 2,2,6,6-tetramethylpiperidyl-4-fulvene (TMPF) on the basis of the reaction (1) is one of the ways of obtaining from this dimer [1]:



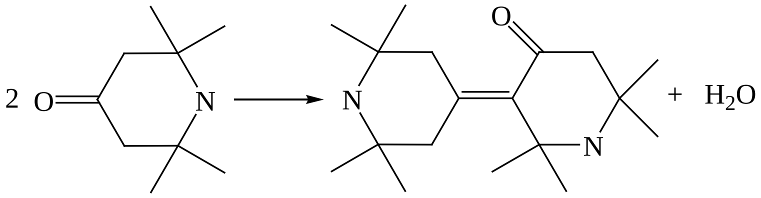
(1)

TMPF dimer indicated high efficiency as a non-coloring light stabilizer and antioxidant for polymers, paints and rubber.

The reaction (1) was carried out in the presence of potassium hydroxide solution in ethanol. The side pathways for the reactant conversions are the reactions of diene synthesis (reaction (2)) and aldol condensation of triacetoneamine (reaction (3)):



(2)



(3)

The rates of the reactions (2) and (3) are almost twice as slow as the rate of the reaction (1) under the conditions of TMPF synthesis. It allows to obtain TMPF with high selectivity and send it dimerization stage without purification.

The influence of potassium hydroxide concentration on the conversion and the initial rate (W_0) was investigated. The curve $W_0 = f(C_{KOH})$ has a straight character up to the concentration 0,15 mol/dm^3 and then tends to a certain limit W_{max}. It is common for the reactions with the formation of an active complex between the catalyst and one of the reagents. The investigation of the effect of temperature at the reaction (1) rate determined the activation energy equal to 112 ± 2 kJ/mol.

1. Shutova T.N. Kinetic regularities of 2,2,6,6-tetramethylpiperidyl-4-fulvene dimerisation / T.N. Shutova, E.A. Surovtseva, G.V. Rybina, S.S. Srednev, I.E. Mohrov // Abstracts of the XIV International Scientific and Technical Conference "High chemical technology 2012", Tula – Yasnaya Polana – Kylikovo Pole, 21-25 May 2012 – Moscow, MITHT, 2012. P. 212 (Rus).

EVALUATION OF GRANULOMETRIC COMPOSITION DYNAMICS WHEN USING “FATTENING” TECHNOLOGY

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The development of overgranulation by pelletizing technology is related primarily to the necessity to obtain pellets of larger size with considerably improved quality coefficient than those to be reached in granulation towers. Melts, solutions, powders with or without a binder may be used for original pellet “fattening”. In this case it is possible to change the composition of the product being palletized or encapsulate the pellets obtained.

Fattening is the process used for overgranulation of original pellets (often produced by prilling and, therefore, not strong enough) with a powder (with or without a binder) by pelletizing in apparatus including those of plate type.

In the course of the process it is necessary to avoid pellet nucleation and their fragmentation. As the process of pellet size gain a random one Fokker-Planck equation is used for description of prill size distribution:

$$\frac{\partial n(r,\tau)}{\partial \tau} = \frac{\partial}{\partial r}\left[-v_+ n(r,\tau) + (D_+ + D_-)\frac{\partial n(r,\tau)}{\partial r} \right], \qquad (1)$$

where v_+ - average rate of prill size variation; D_+, D_-- the fluctuation coefficients of prill size variation rate, n - prill size distribution density, τ - time. The initial condition: $n(r,0) = n_0(r)$; boundary condition: $n(0,\tau) = 0;\ n(\infty,\tau) = 0$; and the normalization condition: $\int_0^\infty n(r,\tau)dr = 1$; the solution can be written as:

$$n(r,\tau) = \frac{1}{\sqrt{2\pi\sigma}} \int_0^\infty \begin{bmatrix} \exp\left[-\frac{1}{2}\left(\frac{re^{(\mu_- - \mu_+)\tau} - 1}{\sigma} \right)^2 \right] - \\ \exp\left[-\frac{1}{2}\left(\frac{re^{(\mu_- - \mu_+)\tau} + 1}{\sigma} \right)^2 \right] \end{bmatrix} n_0(\xi)d\xi, \qquad (2)$$

where $\sigma^2 = \frac{D_+ + D_-}{\mu_- - \mu_+}\left[e^{2(\mu_- - \mu_+)\tau} - 1 \right]$, $\mu_\pm = \frac{v_\pm}{r}$ - the frequency of particle detachment and attachment, $v_\pm$ – prill growth (breakage) rate. The equation (1) is solved by means of numerical and graphical-analytical methods. The approach, which we modified to calculate dynamics of granulometric composition change based on the material balance of the process is possible. In this case it is necessary to solve the equation related to distribution function of granules mass F(m) with distribution function in the beginning of the process given $F_{\text{г}}(m)$ and necessary in the end of the process $F_{\text{гп}}$:

$$\frac{dF(m)}{d\tau} = \frac{1}{\psi \cdot \bar{\tau}} F_{\text{г}}(m) - \frac{1}{\psi \cdot \bar{\tau}}(1+\lambda)F(m) - \frac{1}{\bar{\tau}}(F_{\text{гп}}(m) - F(m)) + \int_0^m \bar{v}(m')\frac{dF(m')}{dm'}dm' - \bar{v}(m)\frac{dF(m)}{dm}m \qquad (3)$$

where τ – time, $\psi = G_{\text{гп}}/G_n$- degree of overgranulation, $G_{\text{г}}$, $G_{\text{гп}}$- mass flow rate of source granules and granulated product; $\lambda = \frac{G_{pn}a_n}{G_{\text{г}}}$ – specific consumption of overgranulating phase; $\bar{\tau} = M/G_{\text{гп}}$ – the average time of stay of granules in the device. The good adjustment of calculation by two given methods and experiment has been obtained.

The results have been obtained within the framework of State task of the Ministry of Education and Science of the Russian Federation.

A THEORETICAL ANALYSIS OF PROCESSES FOR OBTAINING ALKYLDIPHENYL OXIDES

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Many alkyl-aromatic carbohydrates play an important role in the development of contemporary industry and in daily life. Obtaining alkyl-aromatic compounds with the specified characteristics is a promising task for modern day chemistry.

Alkyldiphenyl oxides are used in many fields of industry. They are the basis for creating liquid crystal materials, surfactants, additives for motor oils and much else.

Inevitably none of the production stages for obtaining these substances can be realized without a full theoretical analysis of the process. The main consideration in choosing optimal conditions for obtaining alkyldiphenyl oxides remains the role of thermodynamics and kinetics.

This report discusses the following propositions

- Research has shown that during alkylation of diphenyl oxides by linear Nonenes one can selectively obtain blends of linear ortho- and para-nonyldiphenyl oxides.
- During alkylaton of diphenyl oxides by isobutylene in an Amberlyst 36 DRY catalyst, it is possible to selectively obtain para-tertbutyldiphenyl oxides. Under conditions of achieving equilibrium one can obtain meta-tertbutyldiphenyl oxides.
- Under conditions of effective operation of the Amberlyst 36 DRY, there is a flow up to equilibrium of the positioned liquid phase isomerization of nonyldiphenyl oxides in an aliphatic chain. Under conditions of achieving equilibrium the para-isomers predominate over the ortho-isomers.
- It has been established experimentally that unlike linear alkylbenzoles and alkylphenols, nonyldiphenyl oxides have a characteristic isomerization of the hydrocarbon skeleton in the presence of sulphocationites by the Amberlyst 36 DRY and Tulsion 66 MP. This conversion occurs only in the group of *para*-nonyldiphenyl oxides.
- In the liquid phase, in the presence of a complex based on aluminum halogenides, sulphuric acid and sulphacationite in Amberlyst 36 DRY, we studied the equilibrium of positioned isomerization in the aromatic core of triple-butyldiphenyl oxides. For ten independent reactions in the range 354.9–469.2 K we determined the thermodynamic characteristics. It was established that the total system of transformations is described by a complex of three reactions of the same type.

This work was financially supported by the Ministry of Education and Science of the Russian Federation within the framework of the basic part of governmental tasks of Samara State Technical University (project code 1708).

CATALYTIC HYDRODECHLORINATION OF CARBON TETRACHLORIDE IN A MEDIUM OF SODIUM HYDROXIDE SOLUTIONS

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Carbon tetrachloride, classified as an ozonedepleting substance in the Montreal Protocol, is formed as a byproduct in the production of chlorinated hydrocarbons. To develop a rational method of CCl_4 utilization (an alternative to burning), in this work we study the liquidphase catalytic hydrodechlorination of CCl_4 with the formation of useful products such as sodium formiate, hexachloroethane, and perchloroethylene in the presence of aqueous sodium hydroxide solutions.

Catalysts were prepared by impregnating sibunite with solutions of palladium chloride in muriatic acid and subsequent drying (below 95°C) and reduction (100–300°C) in an argondiluted hydrogen flow. The content of palladium in the finished catalysts sample was 0.5–3.0 wt %. Experiments are performed in a 300 mL autoclave at pressures of up to 1.5 MPa within a temperature range of 80–120°C.

Analysis of the catalyst removed from the reactor along with the reaction mass showed that its particles contained predominantly water with small admixtures of chlororganic compounds. We may therefore assume that the main body of the catalyst was in the aqueous phase. CCl_4 and other organic products arrive to catalyst particles in the form of aqueous solutions. A rise in the concentration of sodium hydroxide in a solution reduces the solubility of both CCl_4, and the hydrogen in it. This slows the rate of the hydrodechlorination of CCl_4 and its conversion.

Investigation of the process allowed us to obtain the rate equation of hydrodechlorination of tetrachloroethane:

$$w_{CCl4} = w_{HCOONa} + 2w_{C2Cl6} \ [mol/(l \cdot s \cdot g_{kat})], \tag{1}$$

$$w_{HCOONa} = 3.3 \cdot 10^{-5} \cdot exp[-(41900 \pm 100)/(R \cdot T) \cdot C_{CCl4} \cdot P_{H2} \ [\mathrm{mol/(l \cdot s \cdot g_{kat})}] \tag{2}$$

$$w_{C2Cl6} = 2.67 \cdot 10^{-1} \cdot exp[-(50800 \pm 120)/(R \cdot T)] \cdot C_{CCl4} \cdot P_{H2}^{0,5} \ [\mathrm{mol/(l \cdot s \cdot g_{kat})}] \tag{3}$$

and of hexachloroethane:

$$w_{C2Cl4} = 2.1 \cdot 10^{-6} exp[-(16200 \pm 45)/RT] \cdot C_{C2Cl6} \cdot P_{H2}^{0,5} \ [mol/(l \cdot s \cdot g_{kat})] \tag{4}$$

where w_{HCOONa}, w_{C2Cl6}, w_{C2Cl4} – the rate of formation of sodium formiate, hexachloroethane, and perchloroethylene, respectively.

Were within the optimum process conditions of hydrodechlorination of carbon tetrachloride: temperature – 110–115°C, pressure – 1.3-1.4 MPa, the concentration of NaOH – 20% by weight., Reaction time – 1.8 hours.

It was calculated that for the optimum system performance, and complete conversion of CCl_4, it is necessary CCl_4 recycled. Maximum performance of the device is achieved after 1.8 hours reaction. When this conversion is 55% CTC, and the organic layer will have the following composition: 72 wt % CTC., Hexachloroethane 11 wt %. Perchlorethylene 16% by weight.

It was developed by a process flow diagram of hydrodechlorination wastes containing carbon tetrachloride.

SIMULTANEOUS IMPACT OF PRESSURE, TEMPERATURE AND LOADING ON SEPARATION PERFORMANCE DURING HIGH-PURITY DISTILLATION

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Distillation under elevated pressure has recently gained popularity for fine purification of liquefied gases and isotope separation, since it allows using of less expensive refrigeration systems reducing energy intensity of the purification process. The increase of pressure also gives an opportunity to raise productivity, since the packing capacity or throughput is known to be increased with pressure. However, carrying out the process under elevated pressures and temperatures leads to a significant change in mass transfer kinetics as well as in phase equilibrium. A complicating factor is the influence of loading affecting hydrodynamics, interfacial area, phase velocities and contact time. In case of elevated pressure distillation carried out at a constant distance from flood the simultaneous impact of increasing pressure, temperature and loading on the overall column separation efficiency should be considered.

The present study deals with the effect of elevated pressure (up to 25×10^5 Pa) on small-scale randomly-packed column separation performance during distillation of high-purity liquefied gases. Examination of mass-transfer performance under elevated pressure at a fixed distance from flood has been made for high-performance spiral-prismatic packings of 4 mm and 2 mm nominal size using silane- and ammonia-based test systems. Simultaneous impact of increasing pressure, temperature and flow rates (loading kept at 80% flooding) on the column separation efficiency has been investigated experimentally and by calculation: pressure dependencies of steady-state column separation factor and the height equivalent to a theoretical plate (HETP) at total reflux conditions are obtained. Observations made demonstrate that the overall column separation efficiency shows an extreme behavior – maximum separation is achieved under specific pressure conditions depending on the variation of the HETP and vapor-liquid equilibrium of the matrix-impurity system. Dependencies obtained are similar both for ammonia- and for silane-based systems and are in agreement with those predicted by analytical method based on empirical correlative approach found in the literature.

As it has been revealed the mass transfer between vapor and liquid phases intensifies with increasing pressure and temperature. Analysis shows that the increase of both liquid- and vapor-side mass-transfer coefficients along with the increase of liquid-vapor contact time associated with the decrease of vapor-phase superficial velocity result in a stable improvement of the overall mass-transfer performance which is represented by the steady reduction of HETP. However, against the background of enhancing mass-transfer kinetics, the gradual reduction of the relative volatility with increasing temperature lowers the overall separation effect. The summation of both sub-factors determines the observed extreme behavior of the overall column separation efficiency under elevated pressure. Simulation of ammonia–acetylene distillation in case of Raschig ring packing showed similar pressure-efficiency behavior under the same operating conditions as for spiral-prismatic packed column. The results obtained and conclusions drawn concerning the general behavior of elevated pressure column separation performance can be applied for optimization procedure defining the optimal operating conditions for distillation of high-purity gases under elevated pressure.

MODERN PROBLEMS OF CHEMICAL TECHNOLOGY OF OIL AND GAS PREPARATION

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Nowadays, the development of most large crude oil fields in Western Siberia is performed at the late stage when chemical reagents are used to stabilize the produced oil.

The investigations carried out to reveal the influence of chemical reagents used in crude oil production showed that the structure of both formation and produced oil becomes changed due to using chemical reagents. As a result, wellstream stability increases and stable water- and oil-containing (oil-in-water, inverted, multiple) emulsions are formed. This may cause technological process failure at oil and water treatment plants.

Well product characteristics are most significantly affected by technological processes of bottomhole zone treatment at producing wells since the chemical reagents injected into a formation, the products of various chemical reactions, mechanical particles formed during rock disintegration, and corrosion products are removed to a greater or lesser extent from the formation. It was found that neither acid nor alkali used for acid or alkaline bottomhole zone treatment is neutralized completely (not greater than by 60–70% in some cases). As both acid and alkaline products are removed, fine dispersions are formed [1].

A variety of bottomhole zone treatment technologies is used today at crude oil fields in Khanty-Mansi Autonomous Okrug to intensify oil influx, to dissolve deposits of asphalts, resins and paraffins, to limit water influx, etc. For this purposes, various inverted emulsions as well as compositions of hydrocarbon solvents and surfactants, polymers, and acids are utilized. Solvents enable producing the large amounts of deposits of asphalts, resins and paraffins which are emulsion stabilizers of natural origin, contained in well products. Highly viscous inverted emulsions, the gel- and deposit-forming compositions, injected for isolating the flooded-out zones, are not completely stable systems and undergo both chemical and mechanical degradation followed by their removal with well products. Synthetic surfactants used for flooding and stabilizing the inverted emulsions enable fine stable emulsions to be formed. Gel-like particles being the agglomerates of water-swellable polymers or high molecular weight surfactants enable the smallest water globules to aggregate around them, which prevents globule integration. Uncontrolled increase of the surfactant amount in oil upon a high flooding and contamination of the formation with mechanical impurities is reported to stipulate the generation of highly viscous stable emulsions both in formation pores and at wellheads. Therefore, decomposition of stable water- and oil-containing emulsions which are supplied to oil treatment plants is still a relevant problem.

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DETERMINATION OF THERMODYNAMIC PROPERTIES BY THE ANHARMONIC APPROXIMATION. LACTONES

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The calculation of thermodynamic properties of substances using relationships of statistical physics and wide temperature range should take into account an anharmonicity of energy levels and conformational variability. We have developed a model "rigid rotator – anharmonic oscillator" (*RRAO*) that considers the convergence of vibrational levels; and the thermodynamic properties of lactones with ring size n from 4 to 8 atoms were computed at 298-1500 K.

The performed conformational analysis showed that four-membered lactone has a planar structure represented by one conformer. Butyrolactone (n = 5) consists of two optical isomers ; valerolactone (n = 6) is realized in the form of an equilibrium mixture of the two isomeric pairs of mirror structures. Caprolactone is a mixture of five conformers, and everyone has a mirror isomer (all are ten structures). Eight-membered lactone consists of thirteen pairs of mirror-isomeric forms.

All found conformers were optimized by B3LYP/6-311++G(3df, 3pd) using program Gaussian 03 in the basis of cartesian spherical functions (6d, 10f). For all conformers the total electron energy (E_{total}), harmonic (ω_{harm}) and anharmonic (ω_{anharm}) frequencies were defined; ω_{anharm} were calculated at the framework of the vibrational second-order perturbation theory (*VTP*2) with quartic force field (*QFF*).

The vibrational energy levels in the our model *RRAO* were calculated by the relation

$$E_i(v) = hc\omega_{harm,i}\left(v+\frac{1}{2}\right) + hc\chi_{i,i}\left(v+\frac{1}{2}\right)^2 .$$

For each mode of every conformer the diagonal constants of anharmonicity matrices and the number of vibrational levels n_{max} were defined.

The mole fractions (χ_i) of conformers for all substances were calculated depending on temperatures by the total Gibbs free energy. Thermodynamic properties of lactones ($\Delta_f H_T^0, \Delta_f G_T^0$, $S°$, C_p) in the range 298.15-1500 K have been found by direct summation on energy taking into account a finite number of levels n_{max} and χ_i (*RRAO*). The expert analysis of known experimental values $\Delta_f H_{298}^0$ have been done and a not temperature term in E_{total} was corrected with the recommended values. It is allowed to obtain accurate values $\Delta_f H_{298}^0$ and $\Delta_f G_{298}^0$ in full temperature range.

To recalculate the existing experimental values of absolute entropy of lactones in the condensed state the vapor pressure of four-and five-membered cycles was measured with a flow method. The good agreement between the experimental and calculated values of $S°$ at 298 K lactones in the gas phase was noted. The correction of enthalpy of formation and Gibbs free energy of the studied compounds were performed by the available experimental data.

THEORETICAL ASPECTS OF SUBCRITICAL TECHNOLOGIES OF ALKYLATION

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Alkylation of aromatic compounds with lower alkenes is one of the major processes of organic synthesis. Realization of alkylation in a special hydrodynamic regime which is characteristic for subcritical conditions will significantly increase efficiency of the process.

For realization these conditions is necessary to consider many aspects, the main of them is the possession of information about temperature level of critical properties for reaction mixture. This aspect is especially important as long as the most efficiently reactions occur in the nearness of the critical point [1]. Subcritical region is defined on one side cricondentherm point, and on the other – cricondenbar. For each mixture the temperature range between of them is individual. Here is an example, for n-pentane + benzene (0.54 mol. fraction n-pentane) mixture temperature range is equal to 13 K, for n-pentane + toluene (0.59 mol. fraction n-pentane) – 63 K and for propylene + benzene (0.59 mol. fraction propylene) achieves 77 K.

In this work we measured the critical temperature of mixtures that typical for alkylation process includes alkanes, alkenes and aromatic hydrocarbons. Prediction methods for critical temperatures and cricondentherm (coexistence maximum temperatures of liquid and vapor phases) for mixtures represented by compounds the above classes were suggested on the basis of own experimental and literature data. The result found to that the systems that presented is benzene (toluene), alkylbenzenes and alkane that concomitant alkylating agent, subcritical region is in the range of 500–600 K. We showed that for alkylation process this level of temperature can be achieved by adiabatic temperature changes during a chemical reaction.

At such temperatures, the formation of subcritical technology alkylation is impossible without considering thermal and thermocatalytic stability components of the reaction mass. Experimentally determined that (C_3-C_4)alkylbenzenes in subcritical temperature ($\leq$573 K) a thermally stable up to 10 hours. Concentration of the catalyst in the reaction mixture at a subcritical alkylation should be minimal to thermocatalytic degradation processes do not occur. For example, for (C_3-C_4)alkylbenzene thermocatalytic destruction of components is minimum at the catalyst ($AlCl_3$) concentration is less than 1% wt.

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THE CHEMICAL BASES OF THE TECHNOLOGY OF OBTAINING 2,4,5-TRIMETHYLBENZOIC ACID

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Durylic (2,4,5-trimethylbenzoic) acid uses in the synthesis of polyester resins and plasticizers, in the manufacture of high strength balloons fiber fabric, and is an intermediate in processes for the production of polycarboxylic acids.

There are known the methods for producing of durylic acid [1] by oxidation durene by oxygen on the cobalt catalyst at 165–170^{o}C, and by oxidation of durene by oxygen in a mixture of acetic acid and acetaldehyde. The yield of the durene taken in the reaction does not exceed ~ 45% [2]. The disadvantages of these methods: low yield of the durylic acid response durene taken in to the reaction; the use of pure oxygen, which increases fire hazard; the carrying away of about 17% solvent – acetic acid with the oxygen, which causes environmentally harmful of these methods.

To expand the resource base, increase the yield of the desired product and simplify the process of its isolation, we proposed the obtaining of the durylic acid by oxidation of the durene by 50–58% nitric acid at a temperature of 30÷50°C and the molar ratio of durene: nitric acid of 1: 10÷16. The process is carrying out at atmospheric pressure.

In such conditions durylic acid is formed by the following reaction:

$$C_6H_2(CH_3)_4 + 6HNO_3 \longrightarrow C_6H_2(CH_3)_3COOH + 4H_2O + 6NO_2$$

Found optimal conditions allow to conduct the reaction with high selectivity, which is not achieved in technologies utilizing higher temperatures. Under these process conditions, by using its exothermicity it is possible to reduce the energy costs for heating the reactor. It was established that at temperatures above 50°C the sublimation of durene and its entrainment with the evolved nitrogen dioxide increase, and at a temperature less than 30°C the reaction time increases considerably, without the increase of selectivity.

Increasing of the amount of nitric acid relatively to durene a noticeable effect on yield of durylic acid does not have. At the same time, as shown by chromatographic analysis, at higher concentrations of nitric acid (more than 60% wt.) along with the oxidation of durene reactions of its nitration and nitrosation proceed, reduced the output of durylic acid and thereby reduced the advantages of the low-temperature regime. The increasing of the duration of the experiment carries out to the oxidation of following methyl groups and dicarboxylic acids formation, which complicates isolation of the desired product, but could be useful for a deeper oxidation.

High yield (72%) and quality (98.8%) of the durylic acid, environmental friendliness and simplicity of the process of obtaining and isolation of the desired product are advantages over existing methods of receiving of durylic aid.

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DETERMINING THE STRUCTURE OF THE DISTILLATION LINE DIAGRAM FOR THE α,γ-DICHLOROHYDRIN–HCl–H_2O SYSTEM

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Ternary vapor-liquid equilibrium (VLE) diagrams provide a graphical tool to predict qualitatively the feasible separations for multicomponent azeotropic mixtures before detailed simulation or experimental study of their distillation. The various graphical representations of the VLE (residue curve and distillation line maps, isotherm map, equilibrium vector field) are closely related and are equally capable of characterizing the mixture.

It is known that in the ternary system α,γ-dichlorohydrin (α,γ-DChH)–HCl–H_2O, there are two binary azeotropes: H_2O-HCl with the maximum boiling point and α, γ-DChH-H2O with the minimum boiling point. Also, possibility of the existence of three-component azeotrope system is mentioned in the literature, but information about composition and boiling point is incomplete. The total information about the ternary system α,γ-dichlorohydrin–hydrogen chloride–water (azeotropy, the boiling temperature of individual substances and singular points) is not available in literature. That is why identification of distillation line map is a difficult task. Improvement of the distillation line map was made on the base of thermodinamic and topological analyses, simulation of vapor-liquid equilibrium on the base of UNIFAC method and experimental work. Simulation of VLE in three-component system: α,γ-DChH–HCl–H_2O was obtained with the help of bundled software ASPEN One®.

Isothermo-isobaric manifold was received on the base of experimental work. Boiling points of ternary systems (α,γ-DChH–HCl–H_2O) were measured accurately at constant pressure using ebulliometer.

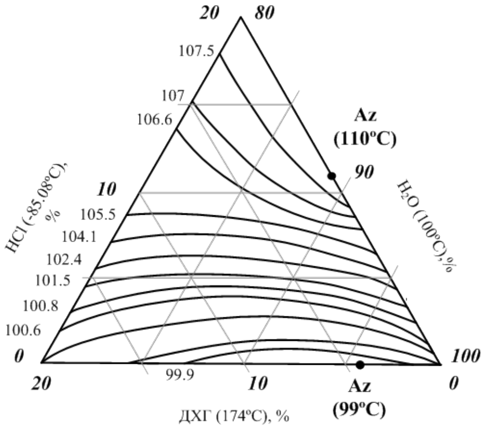

Fig. 1. Isothermo-isobaric manifold (experimental data).

The experimental results obtained (Fig. 1) shows that binary azeotropes are nodes - the stable and unstable. This variant of the location of singular points on the boundaries of the triangle and the isothermo-isobaric manifold occures in the case of saddle singular point existence inside the triangle. Topological class of the ternary diagram – 3.2.1-3a.

Determination of the only one possible location of singular points in ternary system is an important step toward the improvement of technological process of production of α,γ-dichlorohydrin.

ACTIVITY COEFFICIENTS OF WATER IN MIXTURES WITH IONIC LIQUIDS

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The dehydration products of basic and fine synthesis is a frequent problem in chemical industry. This problem usually solved by heteroazeotropic or extractive rectification. Ionic liquids (IL) are considered as alternative separating agents for extractive rectification. The efficiency of ionic liquids is evaluated using activity coefficients of components at infinite dilution (γ^{∞}).

At present there are significant collections (bank) of physical and chemical properties of ionic liquids and their mixtures with different organic substances and water. Data bases include information about the values defined by gas-liquid chromatography. Own experimental experience [1, 2] and analysis of published data revealed some regularities of γ^{∞} for water in the presence of ionic liquids of different nature: 30 binary systems water – ionic liquid in a temperature range from 10 to 95°C.

In 14 systems with increasing temperature γ^{∞} decreases; in 8 systems – γ^{∞} remains practically constant with slight tendency to change. In 8 systems temperature dependence is not fixed. On the example of 23 immidazolium ionic liquids it was shown that increasing (decreasing) of the length of the alkyl radical cation of IL values γ^{∞} increase (decrease). For ionic liquids composed of a certain cation and various anions series, reflecting the influence of the anion on influence on the activity coefficients at infinite dilution were formed.

Revealed patterns are used for the selection of ionic liquids as separating agents and preliminary assessment of their selectivity for the extractive rectification of mixtures containing water.

The results have been obtained within the framework of State task of the Ministry of Education and Science of the Russian Federation.

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Section 2

Advanced Processing at Petrochemistry and Organic Synthesis

APPLYING DIVIDING-WALL DISTILLATION COLUMN FOR EXTRACTIVE DISTILLATION OF BIOETHANOL – WATER MIXTURE

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One of the renewable fuels is bioethanol which is derived from vegetables materials by the fermentation process. The resulting reaction mixture is a mixture contains essentially amount of water and small portion of ethanol. This is azeotropic mixture. However for pure ethanol we must use special distillation methods. One of these methods is extractive distillation (ED).

Authors [1] propose ethanol–water mixture separation by ED with ethylene glycol (EG) as entrainer (E). In [2] considered different methods of this mixture separation in traditional sequence (column of ED and column of regeneration E) and in the system with partially thermally coupled distillation columns (PTCDC). PTCDC reduces reboiler energy consumption for separation up to 3.8% and up to 2.7% in condenser. Besides authors [3] are proposed the using dividing-wall distillation columns (DWC) for improvement energy efficiency of ED. In their opinion this column provides high energy efficiency. We proposed to combine both ideas of authors [2], [3] and constructed ED sequence with DWC.

We have determined minimal energy consumption in reboiler and condenser at optimal parameters in DWC. Data for traditional sequence were obtained earlier in [2]. The number of feed plate and E flow rate were optimization parameters for traditional sequence. The position of inlet and outlet plates of side section, the flow rates of vapor and liquid between the main and side sections of DWC, and the number of plates in main and side sections were the optimization parameters for DWC.

The product purities were fixed as 99.5% for all fractions.

The total number of theoretical trays in system – 34 theoretical trays. Optimal number of theoretical trays in the main column is 30 theoretical trays and in the prefractionator section – 4 theoretical trays.

It was found that the bioethanol – water mixture separation by DWC reduces energy consumption in condenser up to 21% and water circulation flow in condenser and thus reduces condenser dimension.

Work was carried out according to the State task of the Ministry of Education and Science of the Russian Federation # 10.99.2014/K.

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ISOPROPYL ALCOHOL DEHYDRATION IN THE COMPLEX COLUMN WITH REFINING SIDE SECTION

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Isopropyl alcohol (IPA) is widely used as a raw material of paint or ink products and as a solvent in electronic and medicine industries. IPA forms an azeotrope with water at 68.7 mole % and 80.1°C under normal pressure. One of possible ways for the separation of this mixture is to use extractive distillation (ED) with the heavy boiling entrainers such as ethylene glycol (EG) [1] and dimethyl sulfoxide (DMSO) [2]. Conventional ED flowsheet includes extractive distillation and entrainer recovery columns.

Previously we have demonstrated that ED of binary azeotropic mixtures in the one complex column with side refining section leads to the energy consumption decreasing. This system consists of thermally coupling main column and side refining section. The initial feed components are produced as the top products of the main column and the side section; entrainer is recovered at the bottom of the main column. The analogous system decreases the acetone-chloroform mixture ED energy consumption up to 30% [3].

In this work we propose to apply the complex extractive distillation column with the side refining section for IPA-water mixture separation with EG and DMSO as entrainers.

We estimated the thermally coupled extractive distillation system energy consumption and compared them with conventional two columns ED flowsheet ones under optimal values of operating parameters. The total heat duties on reboilers were applied as optimization criteria.

All calculations were done for the separation of 100 kmole/h of binary mixture contained 68.7 mass percent of IPA. The initial feed entered in the column at the boiling point. The purity of products and entrainers was assigned 99.9 mole %. HYSYS is used for distillation simulation and NRTL model is used to predict the activity coefficients. Pressures in columns are equal 101.3 kPa and 20 kPa for ED with EG and DMSO, correspondingly.

Optimization variables include for conventional ED flowsheet the total number of trays, entrainer temperature, entrainer-to-feed ratio, the entrainer and the feed trays locations. For the complex column with side refining section the optimization variables include the entrainer temperature, entrainer-to-feed ratio, the entrainer, the feed and the side outlet trays locations, the flow rate directed to side section.

We compared the energy consumption of flowsheets at the optimal values of operating parameters. It was found that energy consumptions of complex column with side refining section are 4.8% and 4.5% less that ones for conventional flowsheet for ED with EG and DMSO, correspondingly. We had determined that CAPEXs for thermally coupled ED system and conventional ED flowsheet are approximately equal.

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STUDY OF THE DISSOLUTION KINETIC REACTION $CaCO_3$, $CaMg(CO_3)_2$ BY GELLED ACID AT THE PRESENCE OF NaCl

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The acidic treatment of oil- and gas-saturated reservoir with carbonate ($CaCO_3$, $CaMg(CO_3)_2$) matrix is the main method of hydrocarbons inflow intensification. The high rate of concentrated HCl reaction with calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) results in large caverns generation in the bottomhole formation zone. Gelling of HCl (12% wt) solutions improves effectiveness of the treatment. The fundamental investigation of interaction gelled HCl (12% wt) solutions with $CaCO_3$, $CaMg(CO_3)_2$ at high mineralization of water (C_{NaCl} = 150 g/l) has not found. Gelling of HCl (12 % wt) was carried out by biopolymers: xanthan (0,5% wt), sodium alginate (0,5% wt) and surfactant – alkylamidopropylbetaine (6,5% wt) at NaCl = 150 g/l. Viscosity of the solutions was controlled on the rotary viscosimeter HTHP-5550 (Ametek Chandler Engineering, USA) at shear rate gradient 25-100 s^{-1}. Gravimetric method of analysis on the static mode was used for assignment of the interaction kinetic characteristics of acidic solutions with carbonates. The base of method is time registration of carbonate samples mass decrease on the high-accuracy weighing machine. The obtaining relations were approximate by the Avrami equation: $\alpha = 1\text{-}\exp(-k\tau^n)$, where α – sample mass decrease, г; τ – time of the treatment, s; k – the effective rate constant.

The viscosity and kinetic characteristics of interaction HCl (12 % wt) solutions with carbonate core at high mineralization of water (C_{NaCl} = 150 g/l)

Composition of solution	k, s^{-1}		Viscosity, mPa·s
	$CaCO_3$	$CaMg(CO_3)_2$	
HCl (12%)	$12{,}7\cdot10^{-3}$	$9{,}2\cdot10^{-3}$	2,16
HCl (12%) + Surfactant (6,5%)	$0{,}9\cdot10^{-4}$	$0{,}6\cdot10^{-4}$	107,51
HCl (12%) + Xanthan (0,5%)	$1{,}6\cdot10^{-4}$	$1{,}1\cdot10^{-4}$	131,4
HCl (12%) + Sodium alginate(0,5%)	$2{,}1\cdot10^{-4}$	$1{,}5\cdot10^{-4}$	112,78

The viscosity of HCl (12% wt) solution at high mineralization of water (C_{NaCl} = 150 g/l) is 2,16 mPa·s. Gelling of hydrochloric acid increases viscosity of solutions up to 107,51–131,4 mPa·s (table). Gelled acid solutions show apparent viscosity. Reaction rate constants of acid-carbonate interaction were determined when approximating the kinetic relations by Avrami equation. The reaction constants rate turned out various though similar amount of solutions viscosity. High reaction rate was observed when interact hydrochloric acid with carbonates. Gelling of HCl solutions reduces reaction constants rate on order (table 1). Reaction constant rate of dissolution $CaCO_3$, $CaMg(CO_3)_2$ in the gelled acid is significantly lower because of diffusion retardation of H^+ ions to reactionary interface. Maximal retardation of the reaction constant rate was registered when interacting HCl (12% wt) gelled by 6,5% wt alkylamidopropylbetaine. The explanation of received result is lack of the regular spatial lattice with linkage fixed junctions of the line gels, which not produces screening film on the carbonate interface. Thus the reaction constants rate of interaction HCl (12% wt) solutions gelled by xanthan (0,5% wt), sodium alginate (0,5% wt) and surfactant – alkylamidopropylbetaine (6,5% wt) with $CaCO_3$, $CaMg(CO_3)_2$ at NaCl = 150 g/l was determined.

PROCESSING OF BROWN COAL TO PRODUCE WAXES AND CARBON ADSORBENTS

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Complex utilization of energy and chemical potential during processing of solid fossil fuels (SFF) – brown and black coal, schist, turf, is up-to-date challenge [1]. Particular importance has non-fuel utilization of fossil coal producing marketable products which cost significantly exceeds cost of feedstock [2]. One of the most upcoming trend of such brown coal utilization is processing into brown coal waxes and sorption materials with different application.

Current paper presents studies on the influence of preliminary treatment of brown coal on properties and yield of resulting waxes and carbon adsorbents. Efficiency of coal demineralization by solutions of hydrochloric, oxalic and citric acids has been studied.

Samples of brown coal from Tulganskoe, Berezovskoe and Pavlovskoe deposits has been demineralized by solution of corresponding acid with following separation of brown coal wax by extraction in gasoline. Solid residue after extraction has been treated by high temperature carbonization at 800ºC and activation by steam at 700ºC.

It is showed that preliminary treatment of brown coal samples by acids solution results in significant reduction of minerals content. Treatment by hydrochloric acid reduce ash content by 2.2 times in coal from Berezovskoe deposit, by 3.2 times and 3.8 times - in coal from Tulganskoe and Pavlovskoe deposits correspondingly. Treatment by oxalic acid of the same samples reduced ash content for 21, 26 and 40%, and in case of treatment by citric acid ash content reduced by 1.6-1.8 times.

Application of preliminary treatment of coal samples by acids resulted in increase of coal extractibility by gasoline. Maximum yield 15.3% is typical for sample from Tulganskoe deposit treated by hydrochloric acid solution.

Study of waxes properties showed that its acid number differs in range from 16.4 to 24.5 mg KOH/g, and saponification number - in range from 17.5 to 62.4 mg KOH/g which apparently is concerned with significant amount of esters formed during etherification of high-molecular alcohols in waxes by organic acids.

In accordance with complex approach to brown coal processing solid residue after extraction has been treated by high temperature carbonization at 800ºC with following activation by steam at 700ºC.

It is showed that coke yield after carbonization is from 42 to 57% wt., and adsorption capacity by methylene orange for coke derived from extracted coals increased for more than 35% when comparing with coke from initial non-treated coal, and specific surface increased up to 270-300 m^2/g. Activation of carbonated coal by steam results in increase of samples porosity, and specific surface of adsorbents is more than 370 m^2/g with adsorption activity by methylene orange is 304 mg KOH/g.

The results have been obtained within the framework of State task of the Ministry of Education and Science of the Russian Federation.

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PROCESSING OF THE CHLORORGANIC WASTES OF VINYL CHLORIDE MANUFACTURE BY OXYCHLORINATION METHOD

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The chlororganic wastes in the quantity of 25-30 kg per ton of product at the vinyl chloride manufacture are formed.

The perspective method of the wastes utilization is oxychlorination process. The target products are trichlorethylene (TCE) and perchlorethylene (PCE). These are the demanded solvents and the half-finished products in the ozone-safety freons manufacture.

The process can be described by the following reaction (on the example of 1,1,2-trichloroethane which is the main component of wastes):

$$2C_2H_3Cl_3 + HCl + 1{,}5\ O_2 \rightarrow C_2HCl_3 + C_2Cl_4 + 3H_2O$$

The process of wastes oxychlorination is carried out over the fixed bed catalyst – g the cupric chloride on the various supports. Process temperature is 350–400°C. Both the hydrochloric acid or gaseous hydrogen chloride can be used as the chlorine source.

The wastes oxychlorination process was studied over the traditional copper-potassium ($CuCl_2$-KCl) catalysts, which include the supports:

- γ-Al_2O_3 (specific surface 200 m^2/g)
- Support APC: α-Al_2O_3 – 70 %, SiO_2 – 30% (specific surface area 19 m^2/g)

The copper content in the catalysts was 6% wt.

The process was also investigated over the calcium aluminates (cements) prepared by Sci-Ind Association "Azot" (Novomoskovsk). The catalysts contain NiO, CuO, CaO, ZnO, Al_2O_3 in different ratios , the specific surface is from 120 to 130 m^2/g. The catalysts were pre-activated by treatment with hydrogen chloride. As result the copper oxide was converted to $CuCl_2$, which was the main active component in oxychlorination process.

The main results :

- Catalyst $CuCl_2$-KCl / γ-Al_2O_3: 380°C, wastes conversion > 99%, conversion of HCl is 30–50%, selectivity: C_2Cl_4 – 40%, C_2HCl_3 – 35%, CO_x products – 15%.
- Catalyst $CuCl_2$-KCl / APC: 380°C , wastes conversion > 99%, conversion of HCl is 30–60%, selectivity : C_2Cl_4 – up to 50% , C_2HCl_3 – up to 20%, CO_x products – within 1%.
- Calcium aluminates catalysts: 360°C, wastes conversion > 99%, conversion of HCl is 40–50%, selectivity: C_2Cl_4 – 60 %, C_2HCl_3 – 20 %, CO_x products up to 5%.

It was also established that the oxychlorination process does not carried out in the absence of copper compounds.

The maximum yield of the target products (C_2Cl_4 + C_2HCl_3) exceeding 70%, obtained over the a catalyst calcium aluminate having the following composition, % wt: NiO – 26 %, CuO – 10%, CaO – 12%, Al_2O_3 – 52%. Catalyst activity is constant during 25 hours.

The ratio of C_2HCl_3 : C_2Cl_4 can be varied between 1 : 5 ÷ 5 : 1, depending on demand.

FUNCTIONAL MODELING OF VINYL ACETATE PRODUCTION CONTROL

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Vinyl acetate is an essential chemical building block used in a wide variety of industrial and consumer products. It is a key ingredient in emulsion polymers, resins, and intermediates used in paints, adhesives, coatings, textiles, wire and cable polyethylene compounds, laminated safety glass, packaging, automotive plastic fuel tanks, and acrylic fibers. Vinyl acetate is a vinyl ester of acetic acid.

There are 2 production methods for vinyl acetate: the reaction of ethylene and acetic acid with oxygen and the addition of acetic acid to acetylene. The processes can be carried out in the liquid or in the vapor phase. We consider the vapor-phase reaction of acetylene and acetic acid, because it is widely used in Russian chemical industry. Nevinnomysskiy Azot, a part of the EuroChem Group, one of the major producers of vinyl acetate in Russia, uses this method. The production of vinyl acetate consists of the following operations: preparation of raw materials, chemical transformation, condensation of reaction products and purifying by rectification.

Quality management systems are one of the modern ways to improve financial and market performance of the company. The clear and formalized description of the technological, control and test processes is necessary to provide quality management system. We use function modeling methodology for analysis, development and integration of technological and control processes. Functional decomposition provides formal description of the processes, the materials used and their requirements, process equipment, and also the control parameters choice.

At first vinyl acetate production is treated as a single process. Raw materials for this process are acetylene and acetic acid, its results – vinyl acetate and quality certificate. This process is decomposed for five consecutive functional blocks, the first four of them describe the basic technological operations, and the procedure of quality control of vinyl acetate. The sequence of technological operations are described by arrows that specify the "input-output" relations on the functional diagram. Feedback arrows present recycles of raw materials – acetylene and acetic acid. The process of condensate separation is decomposed on the next diagram. Each functional block on the diagram describes the process of separating mixtures into low boiling and high boiling components. It has one input describing a mixture and two outputs – separated products. Rectification column or distillation cubic are the separation mechanism for separating block. Besides vinyl acetate we separate the acetic acid because it can be re-used. The rest separation products are removed from the system as shown by tunneling arrows.

Each separation process, in turn, is decomposed, and processes of quality analysis of the raw materials and/or products and control processes are added. Feedback arrows are used to describe re-use of low-quality products. Control processes are related with technological operations by control arrows.

So, the development of functional model of vinyl acetate production control provides a clear and formalized description of technological processes, quality analysis procedures and control processes. The resulting model is a step in providing information support for the production of vinyl acetate.

FORMAL DESCRIPTION OF CARBON NANOTUBES SYNTHESIS CONTROL

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Carbon nanotubes are promising components of new materials used as reinforcing and functional composites fillers, catalysts, sorbents and accumulators of hydrogen for fuel systems of internal combustion engines, components of electronic devices. Physical and chemical properties of carbon nanotubes differ depending on the purpose of their use. So, if carbon nanotubes are supposed to be used as reinforcing composites filler, their specific adsorption surface and strength are important. These properties, in turn, are determined by the diameter of the tube, the density of their carbon content, degree of the graphitation of carbon and the catalyst. Carbon nanotubes can be synthesized from technological gases, resulting in the process of cracking of liquid organic wastes of chemical and oil-refining industries.

A structured, concise, convenient description of performance of technological and control processes is a condition of effective management of synthesis of carbon nanotubes with the set properties. We use function modeling methodology for analysis, development and integration of technological and control processes. Functional decomposition provides formal description of the processes, the materials used and their requirements, process equipment, and also the control parameters choice. The modeling of carbon nanotubes synthesis control consists of sequential stages: verbal description of technological processes, discovering relations between the nanotubes properties and conditions of their synthesis, sequential processes decomposition [1].

At first carbon nanotubes synthesis is treated as a single process, the input of which are liquid hydrocarbon wastes from chemical and oil-refining industries, and output are carbon nanotubes.

Further, this process is decomposed into 7 main processes: compounding of a liquid phase, analysis of the composition of the liquid phase, cracking, analysis of the composition of cracking gas, carbon nanotubes synthesis, verification of the nanotubes properties, suspension filtration. Among them there are 4 technological and 3 control processes. The control processes are analysis of composition and properties of liquid and gaseous phases. The input of cracking process is the liquid phase, the outputs are cracking gas and suspension. The ‘liquid phase composition’ arrow describes the control relation between ‘analysis of liquid phase composition’ functional block and ‘cracking’ functional block, so it begins as an output and ends as s control. The ‘cracking gas’ arrow from ‘cracking’ functional block to ‘carbon nanotubes synthesis’ describes the input-output relation between the processes. The ‘suspension’ arrow describes the same relation between cracking and filtration processes.

Then we decompose the process of chemical synthesis. The diagram contains of 6 functional blocks, 3 of them describe the technological processes such as gas heating, gas compounding and chemical reaction providing and other 3 are control processes. The control processes describe the choice of synthesis technology, catalyst and temperature. The control functional blocks are related with the technological blocks with ‘output-control’ arrows.

So, we provide a formal description of carbon nanotubes synthesis control by means of functional modeling. The result is the hierarchical structure visual description that is the set of related diagrams.

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THERMOCATALYTIC CONVERSION OF OIL SLUDGE AND BIOMASS

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The oil sludge is dangerous waste of oil-producing and oil-refining industries. The amount of formed waste products can reach up to 5% from produced oil volume. The oil sludge storage in the sludge tanks indicates the irrational usage of fossil minerals. Furthermore the long time stored waste leads to the environment pollution [1].

The peat, wood dust, lignin etc. can be used as the sorbents for the oil removing from sludge storage and for the oil spill recovery. All of them possess the good sorption capacity to oil-products (see table) [2]. The mechanical gathering of sorbent, impregnated by oil, can be realized with excavator or skimmer.

Statistical capacity of biomass regarding to oil

Sorbent	Capacity, kg/kg
Wood dust	4.5-8.5
Peat	8-10
Rice husk	6-10
Cotton sweepings	6-30
Waste paper	8-9.5

The conversion of used sorbent is the most energy- and time-consuming stage of oil sludge utilization. There are various processing methods, which can be combined into the following groups: biochemical, chemical, physical-chemical and thermochemical. Among these strategies, the thermochemical method has many advantages, such as the possibility to process a wide range of organic materials; full waste neutralization; the production of combustible gases and liquids; the production of solid residues, which can be used as the sorbent; no solvent requirement. The most perspective way for waste utilization is catalytic pyrolysis. The use of this method allows producing liquid and gaseous products with high calorific value at low yield of noncombustible byproducts. The use of catalysts allows reducing reaction temperature and increasing the yield of useful products.

In this work the pyrolysis of biomass and oil sludge was investigated. The blend consisted of sand and oil from Caspian field was used as model substrate, and peat was chosen as biomass. The natural and artificially-synthesized aluminosilicates were used as the catalysts. The influence of process temperature, oil sludge composition, the peat moisture content, the nature and amount of catalyst on the pyrolysis products yield and the composition of gaseous blend was investigated.

Temperature is one of the major parameter of pyrolysis, as it affects on the product yield and composition. The optimal temperature of pyrolysis process was 500°C. At this temperature the high yield of gaseous and liquid products with high combustion value was obtained.

The increase of liquid fraction yield by 10% (wt.) in comparison of theoretical value was observed in the case of pyrolysis of blend contained of oil sludge and peat. The use of peat in oil sludge pyrolysis promotes the process intensification, due to mutual positive influence of used blends on the thermodestruction process. The increase of C_1-C_3 hydrocarbons amount in the gaseous products by 10–20% was observed using the aluminosilicates. The artificially-synthesized aluminosilicates – Fe-H-ZSM-5-IE and Fe-H-Mord-20-IE – and natural aluminosilicate – bentonite – have the highest catalytic activity.

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SYNTHESIS OF PROPIONIC ACID BY CATALYTIC HYDROXYCARBONYLATION OF ETHYLENE

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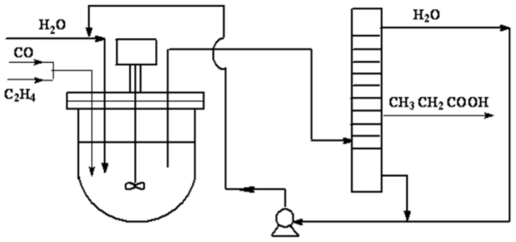
Industrial demand for propionic acid (**PA**) in the eighties for the USSR was estimated ca 250,000 tons per year but factories designed by VNIINEFTEKHIM (All-Union Petrochemistry Research Institution) were not built. **PA** is required for agriculture, paint and varnish, perfume, medical, food industries, plastics fabrication, etc. [1–2].

Some properties of **PA** exceed appreciably the same properties of acetic acid (**AA**), and in some cases it is absolutely irreplaceable. **PA** is not produced in Russia now. Currently the sole process of ethylene hydroxycarbonylation is the BASF method (2 plants in 30,000 tons per year) realized at 250–300°C, 100÷300 at., with low selectivity. Ni $(CO)_4$ is used as a catalyst.

More efficient catalysts for **PA** synthesis as compared with the VNIINEFTEKHIM were designed at the ISMAN by a reaction:

$$C_2H_4 + CO + H_2O \rightarrow CH_3CH_2COOH$$

The reaction proceeds in aqueous propionic acid at 100÷120°C, pressure of 20÷40 at., and selectivity ≥ 99%. The catalysts are propionate, acetate, acetylacetonate, etc. of Pd (II) with stabilizing additives – tertiary organic phosphines [3]. Kinetics and mechanism of the reaction was studied. In addition extended laboratory runs were performed. Technology of the process (see scheme) might be continuous like **AA** synthesis by the Monsanto method but considerably easier owing to the lack of the corrosion-active components (HI, CH_3I).



At 100÷120°C, pressure of 20÷40 at., and [Pd (II)] $= 5 \cdot 10^{-3}$ M the rate of the reaction was 1.0–1.2 $M \cdot h^{-1}$. These data are properly reasonable for a consideration of the proposed method as a base of manufacturing technology.

Authors are ready to any kind of collaboration.

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MATHEMATICAL MODELING OF PROCEDURE RECEIP OF POLYETHYLENE

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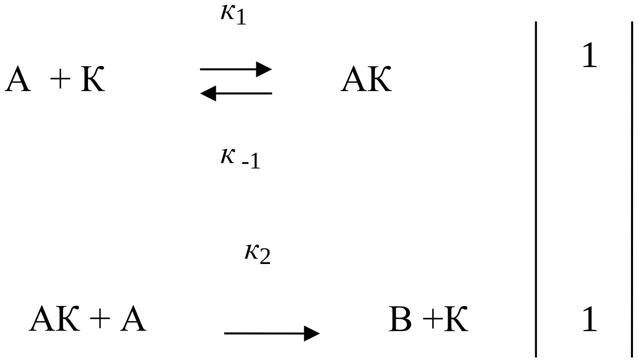
At multitude of chemical causes intermediate particles offer free radical. At course conversion of free radical at relation from cast of a chemical reaction free valence be able take it continue or pass [1]. Thus, at a pattern is coherent conversion of some free radical at the rest:

$$R_1 \to R_2 \to R_3 \to ... \qquad (1)$$

At a brand example may be consider reaction of thermic decomposition (crecing) ethane [2]. Mechanism of polymerization polyethylene from catalyst (K) adds in the formation intermediate catalyst (AK) from ethylene and conversion of that complex at output reaction from extrication catalyst:



$$2C_2H_4 = C_4H_8$$

here B = C_4H_8 – link polymerization. The application of quasistationary approach at these device (at condition $\kappa_2 >> \kappa_1$) allow say of velocity composition of polyethylene across of a concentration reagents and catalyst [3].

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“HYDROPEROXIDE” METHOD OF SYNTHESIS OF 2,5-XYLENOL

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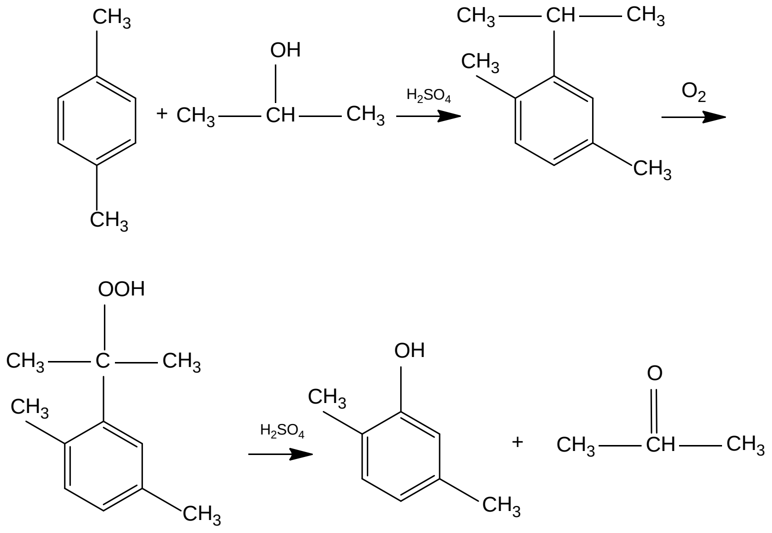
2,5-Xylenol, a large-capacity product of organic synthesis, is widely used in production of plasticizers, paints, vitamin E and heat-resistant materials. Known method of obtaining of 2,5-xylenol have multiple stages and are characterized by low yields of the desired product and the high cost of their preparation. All this greatly limits their commercial implementation.

The most promising and economically preferred method is “hydroperoxide” way of obtaining 2,5-xylenol, which is based on p-xylene. It includes steps of preparing isopropyl-*p*-xylene, its oxidation on liquid phase to the hydroperoxide, and their acidic decomposition to yield the desired products:



The central stage of the “Hydroperioxide” way of obtaining 2,5-xylenol and acetone is liquid phase oxidation of isopropyl-*p*-xylene to the hydroperoxide at a temperature of 140°C, in the presence of 1,19–2,5% of initiator (isopropylbenzene hydroperoxide). The effects of initiator concentration, reaction temperature and duration on the oxidation rate, as well as on selectivity of obtaining hydroperoxide, which respectively amounted to 1-2,5% hydroperoxide/hour and 84–87%, were studied.

The resulting product was subjected to acid decomposition in the presence of concentrated sulfuric acid. 2,5-Xylenol and acetone yield was 75–80%.

SELECTIVE PURIFICATION OF OIL DISTILLATES BY N- METHYLPYRROLIDONE, WHICH CONTAIN CO-EXTRACTANT

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Improvement of the technology of production of petroleum oils is related as to the intensification of basic technological processes oil processing and tar distillates (deasphalting, selective purification of dewaxing solvents), and the introduction of hydrocatalytic processes (hydrotreating, hydrocracking). However, the implementation of the second direction requires significant time and costs. Therefore, without the attention of researchers and trainees is not an option and works aimed at improving the efficiency of established industrial cleaning processes petroleum feedstock.

The aim of this work was to develop a method of intensification oil selective treatment N-methylpyrrolidone. (N-MP). Previously [1] it was shown that the introduction in a basic solvent small addition of co-extractant can regulate its selectivity and / or solubility. This is due to the local change of the molecular force field of the solvent. In this regard, in this work, the influence of low molecular weight alcohols (ethyl-, propyl- and butylalcohol) on the extraction properties of N-MP.

Vacuum distillates and VD-4, which obtained from the distillation of mazut in "Naftan" (Belarus) were subjected to purification. The content of alcohol in the N-MP was 3, 5 and 7 wt%. Results of selective purification VD-4 are shown in the table.

Results of selective oil purification by N-MP and N-MP, which containing co-extractant (t = 50°C; ratio of solvent: feed = 3:1).

Indicator	VD-4			
	–	Ethyl alcohol	Propyl alcohol	Butyl alcohol
Yield of raffinate, % wt	64,2	66,6	65,9	67,9
Extraction Index	1,05	1,50	1,26	1,13
Index of selectivity	1,03	1,05	1,04	1,03

According to the table, quality of selective purification raffinates grows worse with increasing of the length of alkil-radical in the alcohol molecule. These results were confirmed by the structural-group analysis of extract and raffinate, but with the introduction of ethanol additives in N-MP process of selective purification occurs more efficiently than with the selective purification N-MP.

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THE INFLUENCE OF ANTHRACENE FRACTION TO A DEPTH OF THE DISTILLATS' SELECTION DURING THE CRUDE OIL DISTILLATION

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The amount of petroleum distillate fractions obtained under atmospheric and vacuum distillation in industrial plants can be substantially less than the potential content of these fractions in the oil. The problem of most complete extraction of distillate fractions under the distillation of crude oil was solved mainly by the developing of new constructions of contact devices. However, recently methods of physical and chemical technology of the processing of oil dispersions for the intensification of atmospheric and vacuum distillation are suggested[1]. They do not require significant costs and substantial reconstruction of existing AVT.

The aim of this work was to research the influence of additives of anthracene fraction of pyrolysis tar on the yield of distillate fractions under atmospheric and vacuum distillation of crude oil, which is processed into "Naftan" (Novopolotsk , Republic of Belarus). Samples of resin were obtained by the pyrolysis of two types of raw materials: brown coal from Zhitkovichi's deposits (sample 1) and brown coal from Lelchitsy's deposits (sample 2) (table). The content of anthracene fraction in the feed for the distillation was 1.5 wt%.

Feature of anthracene fraction

Indicator	Anthracene fraction	
	Sample 1	Sample 2
The content of pyrolysis tar, % wt.	19,3	38,6
Relative density	0,9226	0,8846
Boiling range, ° C	270-360	270-360
Index of refraction n_D^{20}	1,4913	1,4885

Material balances of distillations, a complex of qualitative characteristics of saturated distillates and samples of oxidized bitumen obtained from oil residues of atmospheric and vacuum distillation of unactivated and activated oil were analyzed during this research.

It was established that the investigated additives of anthracene fractions differently affect upon the depth of the selection of distillates per the raw materials. Anthracene fraction of the sample 1 does not affect upon the yield of the fractions and anthracene fraction of the sample 2 allows to increase the yield of distillates by 5-6%. However, in both cases, there are changes of the distribution of the components of the raw oil system between the saturated oil fractions and the oil residual, as well as improving the quality of oxidized bitumen by increasing the softening temperature, when penetration is almost constant.

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EXPERIMENTAL VALIDATION OF MATHEMATICAL MODEL FOR FIXED-BED FISCHER-TROPSCH REACTOR WITH GRANULATED COBALT CATALYST

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Ficher-Tropsch synthesis (FTS) is a promising technology of natural gas conversion to syncrude. The main FTS problem is scaling of laboratory reactor up to industrial size. Direct scale up is complicated due to coupling of Fischer-Tropsch reactor chemical kinetics with heat and mass transfer limitations in catalyst pellet and catalytic bed as a whole. Mistakes in reactor design may lead to great overheating in catalytic bed and subsequent catalyst deactivation. High precision mathematical model may be an appropriate way to avoid high costs and mistakes in designing scaled-up FTS reactors.

In this study the results of simulation by means of the mathematical model of granulated cobalt catalyst in fixed-bed Fischer-Tropsch reactor are verified with experimental ones obtained from laboratory and scaled-up reactor. It has been shown that for gas hour space velocities over 2400 h^{-1} the results of simulation (CO conversion, liquid hydrocarbon productivity) are in a good agreement with experimental data. The results of this work show that this mathematical model is suitable for scaling-up fixed-bed Fischer-Tropsch reactors.

SYNTHESIS AND PROPERTIES OF SPYROBICYCLIC POLYBROMOCONTAINED N-ARYLAMIDES

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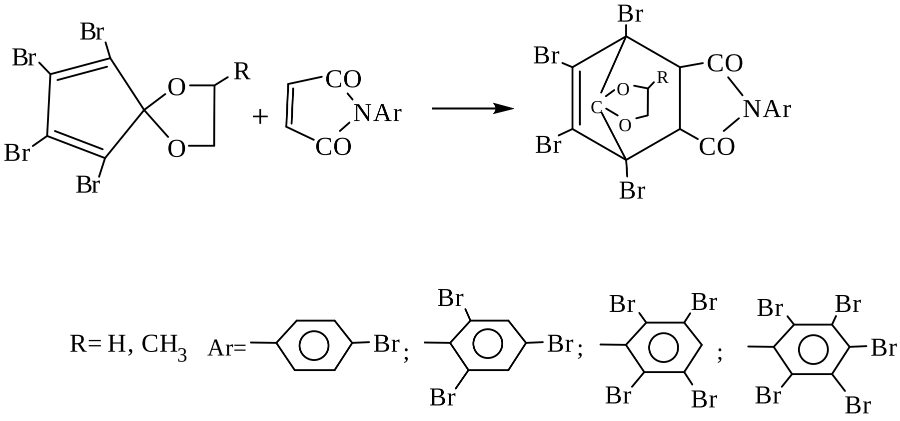
Among the polyhalogencontained cyclic dienes the 5,5-dioxyalkylen-1,2,3,4-tetrabromo-spirocyclopentadienes (TBSCP) are relatively not enough investigated compounds in reactions of diene synthesis, although as dienes and based on them adducts have the theoretical and practical interest.

In order to obtain of the new polyfunctional bromocontained compounds of norbornene range, which have flame-retardant properties, have been studied the reactions of diene synthesis of TBSCP with bromocontained N-phenylmaleinimides in chlorobenzene.



It has been established, that high yields of reaction adducts strongly depended on the reaction conditions. The increasing of incubation time of the reaction mixture, the raising of reaction temperature is contributed to the formation of adducts.

The individuality of the obtained compounds was controlled by thin layer chromatography TLC, and their composition, structure, configuration confirmed by elemental analysis, IR and PMR spectroscopy.

The synthesized polybromocontained spyrobicyclic N-arylamides were tested as a flame retardant for LDPE, MDPE, radiation-modified LDPE and chlorosulphonated PE.

INTENSIFICATION OF PROCESSES OF LIQUID-PHASE OXIDATION OF ALKYLAROMATIC IN THE PRESENCE OF PHTALIMIDE CATALYSTS

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Oxidation of alkyl- and cyclohexylaromatic hydrocarbons underlies promising methods for the production of various oxygen-containing organic compounds, which are widely used in the synthesis of polymeric materials with valuable properties. "Cumene" method of preparation of phenol and acetone and the joint synthesis of styrene and propylene oxide ("Chalcone process") are extensively studied and widely implemented in industry. The main disadvantage of these processes is the low rate of oxidation of hydrocarbons to hydroperoxides. In this regard, the search of conditions of the oxidation process, which would allow to increase the conversion of hydrocarbons to the hydroperoxides, while maintaining high levels of selectivity of their formation is an actual task.

In this paper we proposed to use the phthalimide compounds as catalysts for the oxidation process. During the studies, it was found that the use of *N*-hydroxyphthalimide and its structural analogues as the catalyst allows 1,5-3 fold increase in the rate of oxidation of ethylbenzene and isopropylbenzene, in comparison with the standard industry conditions. The selectivity of formation of hydroperoxides is 90–95%

The scientific and practical basis of "Cymene" process for the preparation of cresols together with acetone, which is based on the use of available raw materials – toluene and propylene (isopropyl alcohol) and known in the petrochemical synthesis technology of liquid-phase oxidation of alkyl aromatic hydrocarbons were developed.

It was found that in the presence of *N*-hydroxyphthalimide, the rate of oxidation of *p*-isopropyltoluene is 8-10 times greater than similar performance achieved previously in the absence of a catalyst. Selectivity of formation of tert-hydroperoxide isopropyltoluene is 90–95% up to a conversion of hydrocarbon of 25–30%. Tert-hydroperoxide isopropyltoluene was separated from oxidation products by extraction with aqueous methanol (efficiency 98%) and was subjected to acid decomposition to form cresol and acetone with a yield of 98% at complete conversion of hydroperoxide.

Along with the improvement of aforementioned process, search for alternative methods of obtaining of large-capacity products of organic chemistry is being conducted. Development of process of joint receiving of (methyl)phenols and cyclohexanone on the basis of oxidizing transformations of cyclohexylbenzene, cyclohexyltoluene, cyclohexylxelyne and isopropylcyclohexylbenzene is of great interest. Influence of various technology factors on the speed of oxidation of these hydrocarbons and amount of the formed hydroperoxide in the presence of the initiator of hydroperoxide isopropylbenzene, and the *N*-hydroxyphthalimide catalyst and its structural analogs was studied. In case of cyclohexyl aromatic hydrocarbons, *N*-hydroxyphthalimide can increase their rate of oxidation of about 2-2,5 times while maintaining high selectivity of the formation of hydroperoxide.

Kinetic regularities of process of liquid-phase oxidation of hydrocarbons in the presence of *N*-hydroxyphthalimide and its analogs are studied, the mechanism of course of reaction is defined, and the role assessment in the phtalimide compounds in the course of liquid-phase oxidation of organic substances to hydroperoxides is given.

STUDYING OF THE COMPOSITION OF HYDROCARBON MIXTURE OBTAINED DURING SUPERADIABATIC PYROLYSIS OF SHALE RESOURSES

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Shale oil is valuable for industrial production. Oil is obtained by thermal decomposition of kerogen - solid organic material located in the shale deposits. During the processing of shale oil a number of useful chemicals are produced, but it`s main part is used as a synthetic alternative fuel source, which is important due to the exhaustion of the world's oil resources [1]. Due to the exigency to improve the technology of processing of oil and gas shale the investigations are carried out in this area. One of the most important stages of the process is the study of chemical composition of shale oil by different analytical methods.

Shale oil samples were obtained by filtration combustion of shale at the superadiabatic mode [2]. Initially, vacuum distillation of original shale oil was carried out in the temperature range 100–250°C. The first fraction was about 10% by volume of the initial resin and contained a large amount of water, which was separated by separatory funnel.

The initial oil and the distillation residue obtained after distilling off the low-boiling fraction were investigated by infrared (IR) spectroscopy. The spectra obtained were virtually identical, because the volume of the distillation residue was about 90% of the original resin. The spectrum revealed bands, which were characteristic for the following classes of compounds: saturated and unsaturated hydrocarbons, benzene homologues, aromatic aldehydes [3]. By elemental analysis the initial oil composition corresponded to the following: C (~80%), H (~10%), O (~10%), S (~0%).

A detailed qualitative and quantitative composition of the first low-boiling fraction was analyzed. Putative organic substances which are presented in the mixture were identified by gas chromatography – mass spectrometry (GC-MS) method using a spectra library. When analyzing data were obtained, we revealed that the sample contained representatives of the following classes of organic substances with the number of carbon atoms from 5 to 12: alkanes, alkenes, alkynes, dienes hydrocarbons, cyclic hydrocarbons, aromatic compounds, polycyclic aromatic compounds, aromatic aldehydes, saturated and unsaturated ketones. Certain functional groups of atoms were identified by the method of infrared spectroscopy. The data of IR spectroscopy confirmed the results obtained during the analysis by GC-MS. Also, elemental analysis of the first fraction was carried out. The structure included the following elements: C (~78%), H (~10%), O (~12%), S (~0%).

Thus, the data obtained could be useful for the following investigations in the area of processing of oil and gas shale.

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“CYMENE“ PROCESS OF OBTAINING CRESOLS AND ACETONE

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Liquid phase oxidation of ethylbenzene and isopropylbenzene to hydroperoxydes and their subsequent transformations underlies the method of obtaining the important products of organic synthesis: phenol, acetone, propylene oxide and styrene.

It is possible to expand this important technical direction of receiving large-capacity products of organic synthesis by using other alkylaromatic hydrocarbons and their hydroperoxides. In this regard, use of closest analog of isopropylbenzene – isopropyltoluene and its hydroperoxide in synthesis of methylphenols (cresols) – valuable organic synthesis products is of great scientific and practical interest. Unfortunately, this way of application of isopropyltoluene and hydroperoxide of isopropyltoluene still not implemented. Above all, this is associated with the formation of a mixture of isomers of isopropyltoluene in the alkylation step, which can not be separated by distillation because of close boiling points. Isopropyltoluene liquid phase oxidation occurs at a slower rate than the isopropylbenzene accompanied by a low selectivity of tertiary hydroperoxyde formation. In this regard, the comprehensive research related to improvement of synthesis of isopropyltoluene, its oxidation to hydroperoxyde, and further utilization is an urgent task.

The fundaments of “cymene” method synthesis of cresols and acetone based on available petrochemical raw materials (toluene and isopropyl alcohol) have been developed.

Found that for the implementation of oxidative method of synthesis of cresols requires the use of wood chemical *p*-xylene and mixture of 40% *p*-isopropyltoluene and 60% *m*-isopropyltoluene, which was obtained by transalkylation of products of toluene alkylation with isopropyl alcohol.

It is established, that isopropyltoluenes oxidation in presence of *N*-hydroxyphtalimide takes place with selectivity of hydroperoxides formation greater than 95% and with a conversion of hydrocarbon of about 25–30%. Under these conditions methyl groups are not oxidized. Tertiary hydroperoxide was separated from the product of oxidation of *p*-isopropyltoluene (with a selectivity of 98%) by extraction with methyl alcohol. It is advisable to use a 30% solution of chloroform in acetone for separation of tret-hydroperoxide, obtained by oxidation of mixture of *m*-isopropyltoluene and *p*-isopropyltoluene.

p-Cresol and acetone was synthesized by acidic decomposition of tertiary hydroperoxyde of *p*-isopropyltoluene in a yield of 95 and 98% respectively. Acidic decomposition of mixture hydroperoxydes of *p*- and *m*- isopropyltoluene proceeds with a formation of *m*- and *p*-cresols mixture (54–58%, 38–40% respectively) with acetone in a yield of 90–95%.

The problems of reuse of the catalyst and unreacted isopropyltoluene were studied. Catalytic role of *N*-hydroxyphtalimide was proved and successful mathematical (kinetic) model of liquid-phase oxidation of isopropyltoluene in its presence was composed.

A block diagram of “cymene” process was composed.

Techno-economic evaluation showed that the cost of cresols obtained using “cymene” method by about 2-3 times lower than the cost of cresol obtained by other methods (methylation of phenol, toluene sulfonic acid alkali fusion, coke-chemical way).

THE HYDROGENATION OF AROMATIC MONONITROCOMPOUNDS ON CATALYTIC SYSTEMS, CONTAINING Pt AND REE OXIDES

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Nowadays the problem of improvement of the technology of amines production is relevant and practically significant and the catalytic hydrogenation with the help of gaseous hydrogen is one of the most important methods of the reduction of aromatic nitrocompounds [1].

The aim of this work is to study the reactions of hydrogenation of aromatic mononitrocompounds (nitrobenzene, *n*-nitrotoluene, *n*-nitrophenol and *n*-chloronitrobenzene) on new catalytic systems, containing platinum and REE oxides. The distinctive feature of the hydrogenation of aromatic compounds on studied catalysts are mild reaction conditions (T = 20°C and P = 1atm), that helps to cutback energy costs and allows to realize the hydrogenation of thermally unstable compounds. The hydrogenation was conducted at the laboratory unit, allowing to determine the reaction rate on the amount of absorbed during the process hydrogen; the progress of the process was followed by the change of potential [2].

For research were used catalytic systems containing platinum and REE oxides and aluminum. As a part of the catalysts was used a full range of REE oxides, except Pm_2O_3. As a comparison catalyst was used 1% Pt/Al_2O_3. The catalysts were analyzed by methods of SEM, XRD, the DTA, TGA. As the environment for hydrogenation of nitrobenzene was taken the water and for hydrogenation of *n*-nitrotoluene, *n*-nitrophenol and *n*-chloronitrobenzene were taken alcohol solutions, previously was defined the area of solubility of the three-component systems «hidrogenating substance – solvent-water». As solvents were used: isopropyl, isoamyl and ethyl alcohols. All substances except of n-chloronitrobenzene absorb the theoretically calculated volume of hydrogen. The degree of conversion for nitrobenzene, n-nitrotoluene, *n*-nitrophenol is close to 100%, while for n-chloronitrobenzene it is only 83%. In connection with speed of hydrogenation compounds can be placed in a row:

nitrobenzene > *n*-nitrophenol > *n* -nitrotoluene > *n*-chloronitrobenzene.

The dependence of activity of the studied catalysts in hydrogenation reactions of aromatic mononitrocompounds from the positions of the elements in the periodic table of D. I. Mendeleev has of extreme character. The most active are platinum catalysts, containing REE oxides, located in the central part of the lanthanide row: Gd_2O_3, Tb_2O_3, Dy_2O_3, the lowest activity have REE oxides, beginning and completing the row of lanthanides (Pr_2O_3 and Lu_2O_3). The use of REE oxides as a part of a catalyst increases its activity in 2.6-6.1 times. Thus, oxides of rare earth elements can be recommended as an integral part of hydrogenation catalysts of aromatic mononitrocompounds. To calculate the kinetic parameters of the reaction was used integral method. The calculations showed that the reaction has the first order on hidrogenating substance. It was found that the relative error of calculation of the rate constants of the reactions of hydrogenation for all investigated catalysts not exceed 5%.

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N-HEXANE TRANSFORMATION ON THE SURFACE OF HIGH-MODULAR SYSTEMS

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The present stage of social development is characterized by the steady growth of oil processing product consumption, increasing requirements to their operational and environmental characteristics. In this connection, the establishment of basic regularities and ways of controlled activation of the C–H bonds in hydrocarbon molecules is a priority lead in the domestic chemical science. ZSM-5-type zeolites find broad application as catalysts of various petrochemical processes and their examination is a perspective direction of oil processing [1–4].

A study was made of n-hexane transformations within a temperature range of 250–500°C. The process of N-hexane transformation was found to include cracking, isomerization and aromatization reactions. The direction of chemical transformations depends on activation parameters and process conditions.

The reactions of catalytic cracking with participation of high-modular ZSM-5-type zeolites were found to proceed by the symmetric mechanism of C–C bond breakage, and by the β-position as well. In this regard, the main products are propane and butane-pentane fraction subject to further transformations, in particular, to isomerization reactions. Detailed chromatographic analysis of the composition of the formed aromatic hydrocarbons indicates the prevalence of toluene and xylenes. This also allows to assume that the formation of aromatic hydrocarbons occurrs due to the reactions of dehydrocyclization of n-alkanes and further alkylation of benzene by the products of cracking reactions to form benzene derivatives.

Table 1. Conversion degree of *n*-hexane and selectivities by basic reaction types, % (cat. ZSM-5, M = 100 mol/mol, activation in air flow, the volume feed rate is 1 h^{-1})

Temperature, °C	250	300	350	400	450	500
conversion degree	36.1	48.6	81.9	97.2	99.7	99.9
selectivity by cracking	38.2	43.3	52.2	54.7	56.0	72.5
selectivity by isomerization	53.7	45.7	36.7	33.2	29.1	11.4
selectivity by aromatization	8.1	11.0	11.1	12.1	14.9	16.2

Table 2. Conversion degree of *n*-hexane and selectivities by basic reaction types, % (cat. ZSM-5, M = 100 mol/mol, activation in hydrogen flow, the volume feed rate is 1 h^{-1})

Temperature, °C	300	350	400	450	500
conversion degree	41.7	65.1	93.0	99.2	99.5
selectivity by cracking	43.1	45.9	57.4	65.2	71.2
selectivity by isomerization	56.0	48.9	35.3	21.8	14.6
selectivity by aromatization	1.0	5.3	7.3	12.9	14.2

Catalyst activation (high-modular ZSM-5-type zeolites) in various conditions leads to redistribution of the active redox centers on its surface, which, in turn, leads to redistribution of the directions of the proceeding reactions. The electivity by aromatic transformations was higher at activation in air flow, and that by isomerization was higher in a hydrogen medium. All the liquid products of transformations possess a high octane number due to the high contents of iso-alkanes and aromatic compounds.

These studies have shown that the high-modular ZSM-5-type zeolites are active in hydrocarbon transformation reactions and can be used as catalysts of various oil processing processes. The reactions of catalytic cracking, isomerization and aromatization are prevailing directions of chemical transformations.

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SYNTHESIS AND RESEARCH OF NEW ORGANIC COMBINATIONS OF NITROGEN AND SULFUR ON THE BASIS OF α-CHLORINE ETHERS OF SOME ALCOHOLS

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232 new organic combinations of nitrogen and sulfur were synthesized on the basis of α-chlorine ethers of some ($C_8H_{17}OH$, $C_{10}H_{21}OH$, CH_3-CCl=CH-CH_2OH) alcohols. New formations of hydrazine, guanidine, diphenylguanidine, diphenylcarbazide, diphenylcarbazone, sulfadimezine, purine and dietiylaminodotiocarbamate containing several -CH_2OR group and a large number of nitrogen atoms were synthesized on the basis of α-chlorine ethers and chlorazone with newly-designed methods for the first time. The contents and structures of the synthesized new organic combinations were identified via know methods (element analyses and IR, NMR and mass spectra).

New formations of phenylhydrazine containing several CH_2OR group and 5; 8; 14 nitrogen atoms were synthesized via firstly used methods. Scientific research works of synthesized new organic combinations was conducted on identification of quality corrosion inhibitor for the steel of «Ст.3» in the electrolyte – hydrocarbon dual-phase environment in the hydrogen sulfide system. It was determined that new formations of organic combinations of nitrogen and sulfur containing various functional group, several CH_2OR group and a large number of nitrogen atoms are the substances with 100 % inhibitor efficiency even in the concentrations of 2.5; 5; 10 mg/l and of high – singnificance from the economic and ecological standpoint.

According to the results of researches, it was determined that inhibitor efficiency and biological activities of the new combinations synthesized on the basis of α-chlorine alkenyloxymethyl ethers are much higher than the efficiencies of combinations synthesized on the basis of α-chlorine-alkyloxymethyl ethers. It was indentified that, synthesized new formations of phenylhydrazine containing several - CH_2OR group and 5; 8; 14 nitrogen atoms are the substances of high effective inhibitor nature in the concentrations of 2.5; 5; 10 mg/l.

According to the results of researches, it was determined that synthesized new organic combinations (35-38) of nitrogen and nitrogen – sulphur with alcoxymethylchlorobutane are corrosion dehydrogenization inhibitors and the substansces prossessing bactericidal property against “Sulfate reducing” bacteria.

It was determined that each of syntesized new formations (39-41) of organic combinations of nitrogen and sulphur composition based on 4-vinyl-cyclohexenone alkoxy-methylchlorinated with α-chlorine esters prossesses effective inhibitor peculiarities for high-efficiency insecticide and acid environment.

New formations of diethylaminoditio-carbamate based on α-chlorine esters, alkoxy-methylchlorinsted 1-methyl and 4-vinyl-cyclohexenine as well as chlorazon were synthesized, for the first time, and highly efficient inhibitor effectivity of each of the very new formations for acid environment was determined. According to the determined results of research work, guarantee for the use of synthesized new organic combinations (mostly, combinations of several -CH_2OR group and nitrogen atoms) of nitrogen and sulphur composition of high effective corrosion inhibitor peculiarities by applying them as high economically and ecologically important inhibitor preparations for protection of technological steel equipment from the corrosion at acid environment in oil and gas production, processing and oil and chemical industry can be considered scientifically substantiated.

According to the results of research work, as some of the synthesized new organic combinations possess peculiarities of high effective biologically active substances, guarantee for the use of the very combinations as bactericide and insecticide preparations is valid.

QUALITY IMPROVEMENT OF CYCLOHEXANONE IN CAPROLACTAM PRODUCTION

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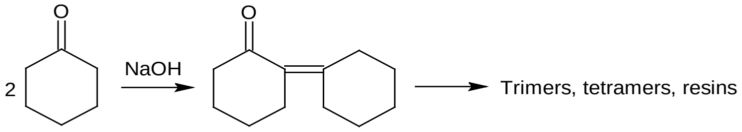
Cyclohexanone is a semiproduct in caprolactam manufacturing, which in its turn is used as a monomer for polyamide-6 production, and there are strict requirements to its quality target. In this regard, a great attention gives to cyclohexanone clearing; the complexity of the process is in a wide range of produced impurities and their small content (10^{-3}-10^{-4} mol/l). The majority impurities contained in the cyclohexanone are esters, aldehydes, alcohols, carboxylic acids, peroxide and unsaturated compounds, formed at the stage of cyclohexane oxidation.

The complex cleaning system allows to improve the cyclohexanone quality indexes: saponification (hydrolysis) of the esters and rectification in the presence of alkaline solutions' small amount. The basic amount of impurities reduces as a result of the esters' hydrolysis reactions (1):

$$ROOC - R' - COOR + 2NaOH \rightarrow NaOOC - R' - COONa + 2ROH \qquad (1)$$

However, as the experience of existing facilities confirms, to remove the ester impurities can be achieved only by 50-70%. In addition, in the presence of alkali there are parallel reactions of the cyclohexanone condensation according to reaction (2), which leads to an increase of its losses (up to 50-100 kg/tonne of cyclohexanone):



(2)

In this investigation are the results of research about the intensification as the saponification process through the use of phase-transfer catalysis and rectification stage by selecting optimal parameters of the process management.

At the research of the saponification process on the model and real systems, the results were obtained during carrying out reactions over an phase transfer catalysts (PTC) and without catalysts. It is established, that high-lipophilic catalyst of trioctylmethylammonium chloride (TOMAC or Aliquat-336) demonstrated the most efficiency in the researched conditions. Its usage accelerates the saponification process in 5-20 times in a concentration-dependent fashion used alkali (5-30%) in comparison with non-catalytic process, allowing to reduce the time of saponification in 2-4 times and side reactions.

At the rectification in the presence of alkali were revealed regularities of competitive reactions behavior (1) and (2), kinetic performances were received, the influence of different concentrations and the methods of alkali feed in the rectification column on the cyclohexanone-rectificate quality were researched.

On the basis of received experimental data are recommended optimal parameters of the esters saponification stage realization in the presence of PTC and the rectification process in the presence of alkali, which allow to reduce the esters in 90-96%, to cut down the high-boiling impurities' formation and to improve the tradeable caprolactam quality to the worldwide standards.

The work has been done with financial support from the Ministry of Education and Science of the Russian Federation within the framework of the basic component of the State task SamSTU (project code: 1015).

SYNTHESIS AND PURIFICATION OF EPOXYCYCLOALKANES FROM PRODUCTS CYCLOOLEFINS OXIDATION BY HYDROGEN PEROXIDE

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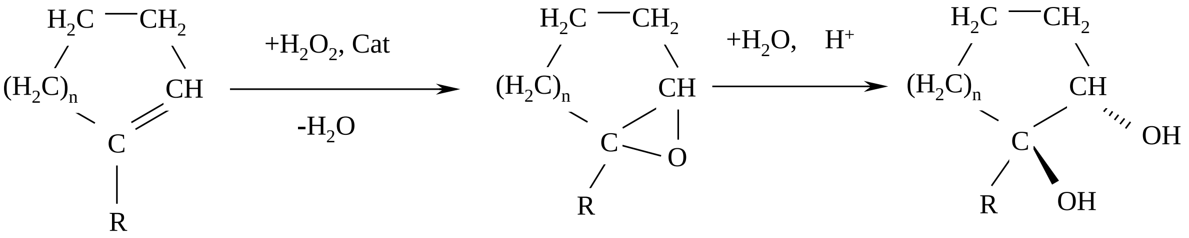
As part of "Green Chemistry", the method of epoxides synthesizing by oxidation of olefins with aqueous hydrogen peroxide was studied. The reaction was carried out in a heterophase system in the presence of solvent, heteropoly compounds of tungsten and a phase transfer catalyst. Advantages of this method are the low temperature of synthesis, an opportunity of use the dilute aqueous solutions of hydrogen peroxide, the high conversion of olefin and the selectivity of desired epoxide.

We were used this method to obtain as 1,2-epoxycyclopentane and 1,2-cyclopentanediol from cyclopentene. The reactivity of cyclohexene, and cyclooctene methylcyclopentyl in this reaction are studied. The conditions allowing to obtain a high yield of the corresponding epoxides were found, and the rates of reaction were determined.



где

R = H, CH_3; n = 1 … 4.

The alicyclic structure of such epoxy compounds provides polymers created on their basis, increased heat resistance and mechanical strength. So, 1,2-epoxycyclopentane was used as the organic component for the manufacture of semiconductor materials, hydraulic fluids, antidepressants.

Epoxycycloalkanes, obtained in a biphasic system with use of aqueous hydrogen peroxide solution, are mainly contained in the organic phase of the reaction mixture and can be separated therefrom by rectification. We were developed a process flowchart of 1,2-epoxycyclopentane purification, which includes three rectifying columns. The purity of the refined epoxide is not less than 99.5%. It has been shown that the similar flowchart of purification can be used for cyclic C_6-epoxides.

However, in the case of 1,2-epoxycyclooctane purification the technological problems arise. Separating the reaction mixture by rectification the C_8-epoxide with the catalytic complex remains in the still kettle of first column. This situation creates significant problems in the organization of the catalyst recycle.

Therefore we propose a method of 1,2-epoxycyclooctane purification from the organic phase of the oxidation products by distillation with the introduction of an additional aprotic solvent. In this case, the catalyst complex in the solution of the solvent remains in the still kettle of column. It allows the catalyst was return in recycle. The epoxide with a part of the solvent as a solution was distilled off and than it was refined by the crystallization. Purity of the obtained product was not less than 99.5%, the contents of water does not exceed 0.1%.

To optimize of purification process we have studied the mutual solubility of the components in water-epoxide-aprotic solvent systems.

PREPARATION AND STUDY OF [$NiCl_2$-$CuCl_2$]/C CATALYST OF METHANOL CARBONYLATION

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In this work, it had been proposed a catalyst for carbonylation of methanol, which increases the efficiency of alternative GTL-processes without the stage of synthesis gas production [1]. We chose the catalyst on the basis of $NiCl_2$ and $CuCl_2$ supported on highly porous carbon. It was selected because $NiCl_2$ has a high methanol conversion index and $CuCl_2$ possesses a significant selectivity towards methyl acetate. Such properties are necessary for carrying out the process of methanol carbonylation in the vapor phase without the addition of precursors. The method of synthesis of the catalyst samples had been described in [2]. We investigated the physicochemical properties of the catalysts and worked out the method for quantitative spectrometric analysis of the elution of the active components from the catalyst surface during its operation.

The properties of the surface of the catalyst samples with different contents of active ingredients were studied by the low-temperature nitrogen adsorption method [3]. Investigated samples have a high specific surface area (500–900 m^2/g) and contain pores with radii up to 20 Å (micropores and small mesopores). It has been revealed that the salts being deposed on activated carbon fill the pores. With the rise of concentration of the salts the pore filling increases, and hence their volume decreases, consequently specific area of the samples also decreases. It could affect the activity of the catalysts.

Preliminary tests of these catalysts showed their effectiveness, however, washout of the catalyst components during the reaction was observed. To estimate the amount of copper and nickel removed from the catalyst during the reaction, the quantitative analysis was carried out by spectroscopy in the visible range.

Initially, the extinction coefficients of $CuCl_2$ and $NiCl_2$ solutions of known concentration had been calculated (ε_{Cu} = at λ_{max} = 817.0 nm and ε_{Ni} = at λ_{max} = 394.3 nm). Then the concentration of washed out $CuCl_2$ in the solution after carbolanylation reaction was determined (C_{Cu} = 0.137 M). However, we couldn't determine the concentration of washed out $NiCl_2$ because it was too low (the maximum of the spectrum of washed out solution was very negligible). Therefore, the method of UV-VIS spectroscopy can be applied only for the determination of amount of $CuCl_2$ removed from the catalyst during the reaction.

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MECHANISM OF PYROCARBON FORMATION ON THE SOOT PARTICLES SURFACE

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Regularities of soot specific surface changing in the process of pyrocarbon formation is examined and mathematical models described this process is given. It is shown that experimental results satisfactorily describe the model supposing formation local pyrocarbon clasters and their unification into the united layer. On the base of these results the hypothesis of pyrocarbon formation mechanism on the soot particles surface is proposed.

Hypothesis is proposed adsorption of the formation products from gas phase on the active centers; carbonization of these products with the formation pyrocarbon clasters; clasters`s growth and their unification into the united layer of pyrocarbon.

It is offered that defects of crystal lattice of substrate that are formed on the borders contacts of crystallites may be such active centers.

To confirm this hypothesis there were made experiments with the soot samples N220 and N234. These samples differed from each other diameter of soot particles and they were undergo graphitation for the crystallites size changing. (N220gr and N234gr).

It is shown influence of crystallites contacts borders length of substrate on the pyrocarbon formation rate in the table.

Influence of crystallites contacts borders length of substrate on the pyrocarbon formation rate

Sample of the soot	Middle diameter of soot particles, nm	La size, nm	Crystallites contacts borders length*, nm	Rate of pyrocarbon formation, g/(min*m^2)
N220gr	27	7,6	1200	1,9*10^{-5}
N234gr	32	7,5	1700	2,1*10^{-5}
N220	27	3,2	2900	6,1*10^{-5}
N234	32	3,1	4100	7,8*10^{-5}

*Crystallites contacts borders length is calculated by dividing the soot particle surface by the crystallite area followed by multiplication by its perimeter.

It is shown that products of pyrocarbon formation are adsorbed in the place of heteroatom’s localization and functional groups of substrate. These places are also active centers of pyrocarbon formation beginning.

TECHNOLOGICAL ASPECTS OF PRODUCTION OF O-SILYLURETHANS AND UREAS

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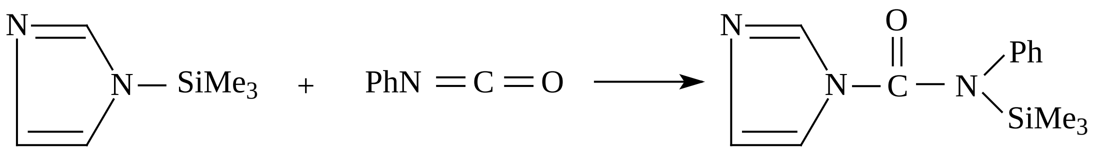
O-Silylurethans, silicone containing urea and semicarbazide for a long time are of great interest of the scientists, because of their high reactivity and continuously increasing applied value of the compound classes.

Previously we have reported of our new one-pot method of obtaining O-silylurethans containing diazole, which involves the implementation of two consecutive reactions occurring in the same reactor without isolation of intermediate products.

We have developed the technological fundamentals of obtaining N-silylsubstituted urea, containing diazole and N-silylsubstituted semicarbazide.

It is established that 1-(trimethylsilyl)-1H-imidazole easily reacts with phenylisocyanate, which results in obtaining previously unknown N-phenyl-N-trimethylsilyl-1H-imidazole-1-carboxamide (I).

Scheme 1

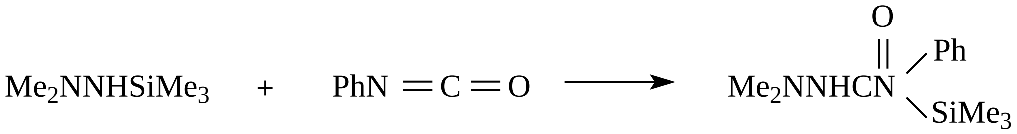


I

The reaction was carried out without the use of a catalyst, in the process of mixing the reagents was observed heating of the reaction masses up to 40^0C, the yield of product (I) was 100%.

Reaction of N,N-dimethyl-N`-trimethylsilylhydrazine with phenylisocyanate also accompanied with an exothermic effect and leads to the formation of a previously unknown N-silylsubstituted semicarbazide (II).

Scheme 2



II

In this case the catalyst is also not used, in the process of mixing the reagents was observed heating of the reaction masses up to 38^0C. The yield of 2,2-dimethyl-N-phenyl-N-(trimethylsilyl)carboxamide (II) was quantitative and 100%.

It should be noted that the obtaining of N- silylsubstituted urea (I) and N- silylsubstituted semicarbazide (II) was done bypassing an additional heating step, and the time of synthesis of the compounds (I) and (II) does not exceed 30 minutes.

AN INVESTIGATION OF V_2O_5/γ-Al_2O_3 CATALYSTS FOR CHLOROBENZENE TOTAL OXIDATION

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The destruction of halogenated organic wastes from chemical industry is an important component of environmental compliance. This is often achieved through some form of thermal process such as controlled high-temperature incineration, fume incineration and regenerative thermal oxidation. These process, require very high-temperatures, usually on the order of 1000–1200^{o}C. An alternative approach is to utilize catalytic oxidation. High efficiency of catalytic oxidation can be obtained at much lower temperatures conditions in the range of 300–500°C are typical.

Vanadia based catalysts find widespread application in industry mainly for partial oxidation. At the same time V_2O_5 based catalysts have shown the highest activity for total oxidation, which is also affected by the nature of support [1].

This paper examines the use of γ-Al_2O_3 as support for V_2O_5 based catalyst in the total oxidation of chlorobenzene. Alumina was prepared according to the scheme bayerite – boehmite – gamma alumina, the method of synthesis is shown in [2]. V_2O_5/γ-Al_2O_3 (5 wt. % of vanadium) based catalyst was elaborated by impregnating γ-Al_2O_3 with NH_4VO_3 as precursor. Specific surface area of the catalyst sample is 115 m^2/g.

Catalitic oxidation was performed in a flow-through tubular quartz reactor. Experimental conditions: temperature interval 250–500^{o}C, the catalyst volume 4 cm^3, chlorobenzene concentration in the feed of 0.7 vol. %, feed space velocity of 2000 h^{-1}, and fourfold excess of oxygen.

The composition of the oxidation products and the chlorobenzene content in the starting mixture was determined with an LKhM-8MD and a Kristall-2000M gas-liquid chromatographs and with an Agilent Technologies 6890N/5975 gas chromatograph-mass spectrometer.

The total oxidation of chlorobenzene starts at 320^{o}C, whereas thermal decomposition of chlorobenzene under the above-indicated experimental conditions on γ-Al_2O_3, as well as in the reactor without catalyst, is observed only at temperatures exceeding 450^{o}C. The degree of conversion of chlorobenzene at the catalyst did not exceed 70% at 500^{o}C, selectivity with respect to CO_2 was 11%.

In chlorobenzene transformation products, along with CO_2, we identified by gas chromatography-mass spectrometry 1,3,5- (or 1,2,3-, or 1,3,4-) –tri-chlorobenzene, 1,2,3,4- (or 1,2,3,5-, or 1,2,4,5-) –tetrachlorobenzenes, pentachlorobenzene, and hexachlorobenzene in trace amounts. Perhaps these products originate from chlorobenzene disproportionation.

This work has been performed with financial support of RFBR, project No. 14-03-00630_a.

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ECONOMICAL EFFECTIVENESS OF DIVIDING - WALL DISTILLATION COLUMNS FOR EXTRACTIVE DISTILLATION

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Esters are widely used in industry as solvents. Etherification is more common method of esters production. Usually the esters formed azeotropic mixtures with the products and reactants, and an extractive distillation process (ED) is used for esters recovery. There are two possible variants for realizing this process. The first way is to use reactive distillation column. Another way is to use system consist of common reactor and distillation columns. Traditional ED sequence consists of extractive distillation column and entrainer regeneration column.

In the article [1] partially thermally coupled distillation column (PTCDC) is proposed for separation of such mixtures. The comparison was made between traditional sequences and PTCDC in energy efficiency. We estimated the effectiveness of ED in dividing – wall distillation columns (DWC) which were constructed as PTCDS. We investigated the separation of some industrial mixtures of esters and alcohol such as methyl acetate (MeAc) – methanol (METH) (I), ethyl acetate (EAc) – ethanol (ETH) (II) and isobutanol (IB) – isobutyl acetate (IbAc) (III). Ethylene glycol (EG) as entrainer was used for ED of I. Propylene glycol (PG) as entrainer was used for ED of II. Dimethylsulfoxide (DMSO) as entrainer was used for ED of II. Butyl propionate (BUP) as entrainer was used for ED of III. N,N-dimethylformamide (DMF) as entrainer was used for ED of III.

PTCDC flowsheet for ternary mixtures separation was developed in [1]. It provides energy consumption reduction in compare with traditional sequence. Some data show a difference in energy efficiency of investigated PTCDC [1].

We carried out a computation and comparative analysis of capital expenditure (CAPEX) for separation of these mixtures in traditional ED sequence and in PTCDC. Data for CAPEX calculation were taken from [2].

Computation results are shown in the table:

Mixture	Q^{reb}_{Trad}, kW	Q^{reb}_{PTCDS}, kW	ΔQ^{reb}, %	CAPEX, $ (Tray Tower)		Δ CAPEX,%
				Traditional ED	PTCDC	
EAc-ETH-PG	6719,7	6541,1	−2,7	156021	153615	−1,6
EAc-ETH-DMSO	2882,1	2812,2	−2,4	95005	97047	+ 2,1
IB-IbAc-BUP	1050,7	839,4	−20,1	146639	130435	−12,4
IB-IbAc-DMFA	1226,2	868,0	−29,2	156484	149463	−4,7
MeAc-METH-EG	7513,5	7407,3	−1,5	156021	150477	−3,7

Thus we obtained the data which indicate that CAPEX for DWC are equal or less than for traditional ED.

Work was carried out according to the State task of the Ministry of Education and Science of the Russian Federation # 10.99.2014/K.

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ADVANCED MACROPOROUS CATALYSTS FOR HEAVY TATAR OIL REFINING

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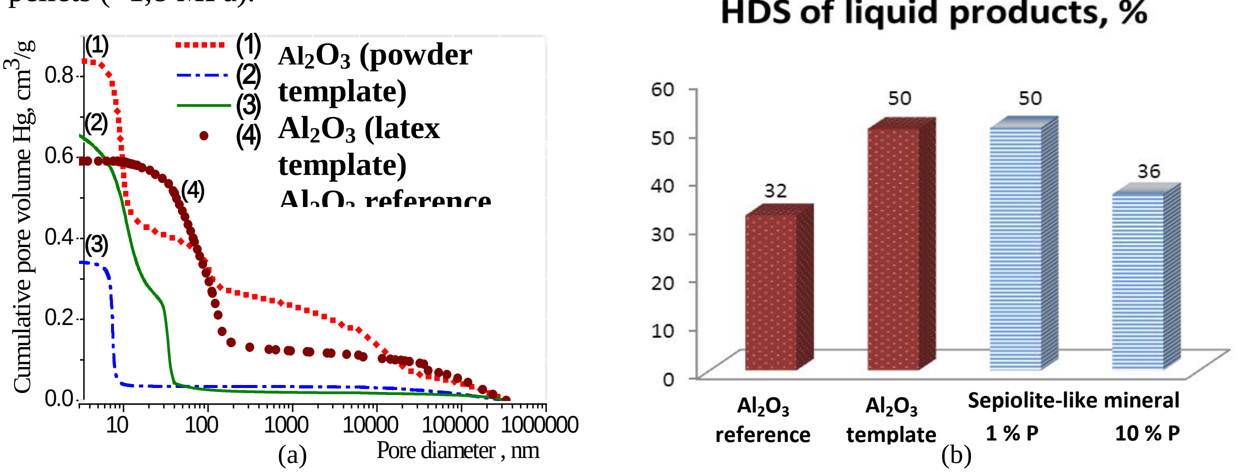
Hydrotreatment of heavy feeds seems to be more feasible in long-term outlook as they provide valuable products without large amounts of coke, having limited market demand. However, special attention should be given to removal of S-, N- and metal impurities because of an environmental hazard, poisoning of hydrocracking catalysts and deactivation of the refining equipment.

In this work enhanced CoNiMo catalysts for heavy oil treating with improved textural and acid-base properties were proposed. Macro-mesoporous γ,δ-alumina with advanced texture and natural sepiolite-like mineral, resistant to deactivation due to the pronounced basic properties, were employed as the catalyst supports.

Template method, using latex or powder of polystyrene micro- or nanobeads, was proposed for preparation of macro-mesoporous alumina. All the samples, obtained by this technique, exhibited high specific surface area (160-180 m^2/g) and pore volume (0.6-0.8 cm^3/g), as well as a bimodal pore size distribution with maximums at 10 and 50 nm (Fig. 1, a). The sepiolite-like mineral had low surface area (20 m^2/g) and a multiphase composition, represented mostly by MgO (~55%) and $Ca_3Mg(SiO_4)_2$ (~40%) after calcination at 800 ^{o}C. For tuning its basic properties the sample was modified with phosphoric acid. The catalyst synthesis was carried out via wetness impregnation with bimetallic citric complex $CoNi[Mo_4(C_5O_7H_5)_2O_{11}]$ followed by soft calcination and sulfidation.

The catalysts obtained were tested on hydrodesulphurization (HDS) and hydrodemetalization (HDM) of heavy oil in Berty stationary basket reactor under conditions similar to industrial ones (380–420^{o}C, 70–150 MPa, H_2/feed volume ratio 1000, LHSV 0.50–0.89 h^{-1}). Heavy tatar oil characteristics were as follows: gravity 14.75^{o}API, viscosity 3.6 St at 25^{o}C, S 3.4 wt. %, V 2700 wt.ppm, Ni 1100 wt.ppm.

It was clearly shown that templated alumina based catalysts performed higher HDS (by 56%) and HDM (by 40%) activity compared to traditional ones, while sepiolite-based catalysts exhibited surprisingly improved efficiency in sulfur removal (Fig.1, b). The HDM activity was proved to be mostly affected by pore volume of the catalyst, having the highest value (68%) for templated samples. Thus, the proposed catalysts seem to be prospective for heavy oil refining due to its high efficiency, relatively low precursor costs and high crush strength of catalyst pellets (>1,8 MPa).



(a) (b)

Figure 1. (a) Hg porosimetry data for all samples used, (b) HDS conversion of heavy tatar oil.

CATALYST BASED ON HLaY – ZEOLITE AND MONTMORILLONITE PILLARED BY ALUMINIUM IN THE CRACKING OF HEAVY VACUUM GASOIL

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The composite which is a zeolite supported on aluminum pillared Tagan natural montmorillonite Al (2.5) NaMM was studied as a component of the cracking catalyst of a vacuum gasoil. A support of zeolite on nanoscale pillared clay promotes the retaining of the thermal stability of the contact. Matrices based on pillared clays exhibit plasticity and high strength properties. According to the data obtained on a universal testing machine, Autograph AG- 100 GOST 8817–82 kNX «jumping-up test method» granules of synthesized catalysts withstand loads of up to 306 kg/cm^2.

The catalyst with composition of HLaY + Al (2.5) NaMM with lanthanum content of 1-1.2 wt.% was tested in the vacuum gasoil cracking of Pavlodar Petrochemical Plant (PPCP) with ebp 560°C. In the table the activities of the catalyst are compared before and after steam treating (s/t) during 6 hours 750°C with 100% steam.

Material balance cracking of PPCP VG at the different temperatures

Product yields of cracking (wt %)	Before s/t		After s/t	
	500^0C	550^0C	500^0C	550^0C
Gas	3	19,3	3	5
Gasoline	17,0	20,5	7,9	25,5
Coke	7,8	2,3	9,8	10,0
Light gas oil	55,0	45,3	72,0	52,1
Residuum	10,0	5,0	5,5	5,4
Wastes	7,2	7,2	2	2
Conversion	83,0	88,0	92,7	92,6
Sum of the light products	72,0	66	72,9	77,6

Gasoline yield in VG cracking of PPCP after steam reforming at 550°C increases from 20.5 till 25.5% and decreases at $T_{critical}$ = 500°C from 17.0 till 7.9%. Steam reforming of contact leads to a significant increase in the yield of light gas oil at 500° and 550°C, sum of light products (up to72, 9% and 77.6%) and the conversion of VG (up to 92.7% and 92.6%).

The product of cracking of VG PPCP contains 32.9% paraffin-naphthenic hydrocarbons, 21.9% iso-products, 22.1% aromatics and 0.4% oxygen containing compositions after 500°C s/r. The rising of cracking temperatures leads to a higher yield of aromatic hydrocarbons' up to 30.4%. The gasoline octane number corresponds to 75, the saturated vapor pressure is 19.9 kPa, d = 759 kg/m^3. Temperature of SBP is – 42°C, the 20% gasoline is distilled at 81°C, 50% – at 127.6°C, 70% – at 158.3°C and 95% – at 191°C.

The constancy of activity of the catalyst after steam reforming indicates a high thermal stability of the catalyst. Availability of preparation of the catalyst matrix, high yields of light gas oil, the sum of light products and high conversion of VG allow us to consider composite as a perspective component of a catalyst for VG cracking.

TECHNOLOGICAL ASPECTS OF PRODUCTION OF UREAS USING ORGANOSILICONE ISOCYANATES

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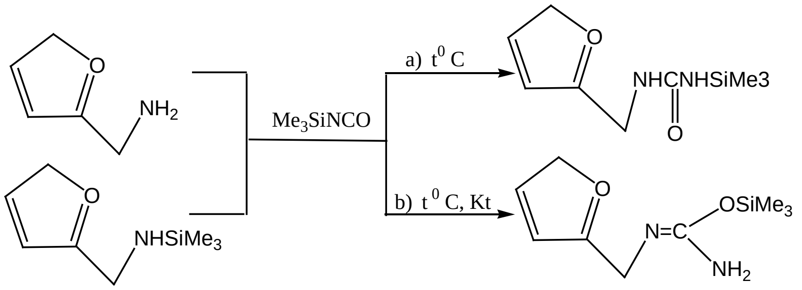
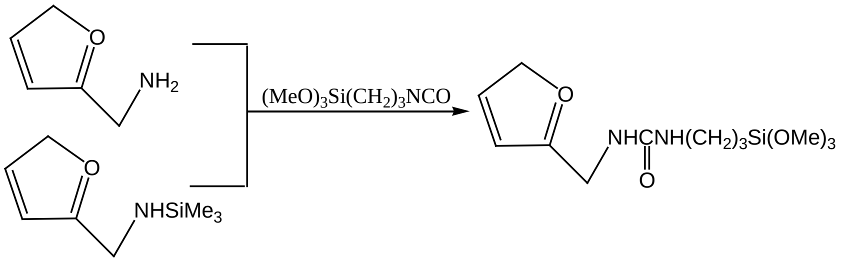
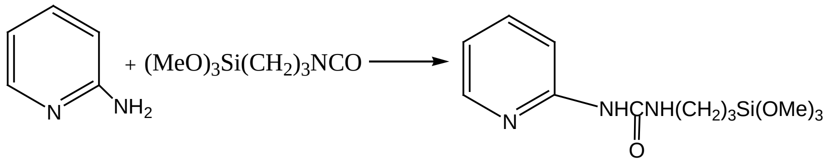
It is stated that alternatively to organic isocyanates, their organosilicone analogues behave a little bit differently in the reactions with amines and aminoalcohols.

For example, trimethylsilylisocyanate interacts with 2-furylmethylamine and it`s trimethylsilyl derivative only while heating (reaction a – 1h, 100–110ºC; reaction b – 65h, 80ºC) or using catalytic quantities of bis((2-ethylhexanoyl)oxy)stanium (reaction b).



Using of (3-isocyanatopropyl)(trimethoxy)silane also finishes by creation of ureas. The process is carried out exothermically irrespective of using 2-furylmethylamine, either it`s trimethylsilyl derivative or aminopyridine or 2-((trimethylsilyl)oxy)ethylamine.





$$Me_3SiOCH_2CH_2NH_2 + (MeO)_3Si(CH_2)_3NCO \longrightarrow$$

$$\longrightarrow Me_3SiOCH_2CH_2NHCNH(CH_2)_3Si(OMe)_3$$

The results have been obtained within the framework of State task of the Ministry of Education and Science of the Russian Federation.

LIQUID PHASE ISOMERIZATION OF ALKENES

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Increased consumption of motor fuels of improved quality has accelerated the use of unsaturated hydrocarbons to produce high-octane gasoline components. One of trends in such technologies development is oligomerization of alkenes. Modern catalysts make effective liquid-phase cold oligomerization processes possible. The question is what should be the requirements to the composition of the raw materials. This depends upon the type and depth of isomerization in the system.

A special place in petrochemical processes is held by alkylation of aromatic substrates of different nature. Based on them different additives (with different functionality) to oils and fuels, monomers and auxiliary materials for polymer chemistry, organic semiconductors, surfactants, fragrances, etc. are produced. Alkenes arte solely used as alkylating agents, and quality of the products obtained is directly connected with the type and depth of isomerization in the system.

In this paper we review liquid phase isomerization of branched hexenes, linear and branched octenes, branched dodecenes as well as tetradecenes on sulphocationites of different brands with the use of model systems. Selected systems allowed not only to selectively review alkenes isomerization as such, but to establish the role of these transformations in formation of reaction mass composition in oligomerization of alkenes as well as alkylation of benzene, phenol and diphenyloxide.

Thermodynamic analysis of these processes and the results of kinetic studies served as a basis for assessment of the relative role of geometrical and skeleton isomerization of alkenes under liquid-phase processes on sulphocationites.

The results have shown, that:

Isomerization of branched octenes between 293–373 К is observed with achieved equilibrium in the system of 2,2,4-trimethylpentene-1 and 2,2,4-trimethylpentene-2. In the process of phenol alkylation by the branched octenes, competing reactions of oligomerization, isomerization as well as alkylation occur. When phenol/olefin ratio is 2/1 mole/mole, equilibrium between alkene isomers is reached, isomerization rate is higher that alkylation and oligomerization rate; when phenol/alkene ratio is increased – isomerization equilibrium is not reached.

Isomerization of 4-methylpentene-1 (4-МП-1) is observed with formation of 2-метилпентена-2 and 4-methylpentene-2 (cis and trans). With time and temperature increase cis-isomer concentration tends to zero. At 363 К 4-МП-1 converts almost completely to isomers within 3.5 hours. During phenol alkylation by 4-methylpentene-1, the observed trends persist except that 2-methylpentene-2 formation rate is lower than alkylation rate.

On sulphocationites, which have been studied, skeleton isomerization of alkenes is slightly observed. Octene-1 promptly gives equilibrium mixture of all linear isomers regardless of the medium (hydrocarbons, phenols, diphenyloxides) properties.

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ALKENES OLIGOMERIZATION

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Catalytic reforming is the basic process for motor gasoline production in Russian oil refining industry. At present production and use of alkylate, isomerizate and oxygenate as high-octane number components is not widespread. Increasing oil refining depth at Russian refineries leads to increased production of gas fractions, but modern structure does not allow the refineries to fully process the produced alkenes. Development of oligomerization process can serve as a solution to this problem. Oligomerization technologies by leading global companies, such as (Platforming), Neste Oil and Kellog Brown & Root (NExOCTANE), Axens (Selectopol and Polynaphtha), «Süd-Chemie» («COD»), Saipem (Iso-OctEne) have become a frequent practice recently. Modern catalysts make effective liquid-phase cold oligomerization processes possible. The question is how to provide required quality of the products obtained at minimum cost; and this depends upon oligomerization ans isomerization type and depth. The main emphasis of this paper was made on liquid-phase oligomerization of branched butenes, pentenes and octenes on sulphocationites of different sorts.

The results have shown, that:

In the range of 273–333 K maximum selectivity of the process with respect to dimers reaches 92, 83, 95% with Amberlyst 36 Dry, Lewatit K 2640, Tulsion 66 MP at isobutene conversion rate of 41, 53, 40% correspondingly. For Amberlyst 36 Dry and Lewatit K 2640 temperature increase is accompanied by formation of isomers other than 2,2,4-trimethylpentene-1 and 2,2,4-trimethylpentene-2, for Tulsion 66 MP these transformations are less signified.

On all catalysts accumulation of dimers promotes their dimerization to form tetramers. At 323 K on Amberlyst 36 Dry tetramers content reaches 77% with 1% trimers. Upon reaching 373 K destruction of tetramers with elimination of isobutylene and formation of trimers becomes significant.

Oligomerization of isobutylene is accompanied by formation of tert-butyl alcohol. The effect of water and alcohol on selectivity and conversion has been studied. Reduction of tert-butyl alcohol concentration less that 10% increases tri- and tetramers. With further alcohol content increase tri- and tetramers are not formed, and alcohol content less than 10% in the system reduces oligomerization rate in more than 3 times.

Unlike isobutylene, oligomerization of isoamylene with Amberlyst 36 Dry at 313–353 K proceeds more selectively with the formation of dimers in the conversion of original alkene reaching 90%. Temperature increase is accompanied by mutual transformations in group of dimers; their subsequent oligomerization is poorly expressed. Water and alcohol, compared to isobutylene, have less effect on selectivity and conversion.

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OXYDATIVE CHLORINATION OF METHANE UNDER THE PRESSURE

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Currently there are a number of perspective industrial processes of olefins obtaining from natural gas: the process "methanol-to-olefins" (MTO), the Fischer – Tropsch process, and the process of the methyl chloride catalytic pyrolysis, as follows:

$$n\,CH_3Cl \rightarrow C_2H_4 + C_3H_6 + C_4H_8 + \text{other hydrocarbons} + n\,HCl;$$

The method of methane oxidative chlorination is used for methyl chloride producing and recycling of the resulting hydrogen chloride:

$$CH_4 + HCl + 1/2\,O_2 \rightarrow CH_3Cl + H_2O.$$

As a result, the process is balanced by chlorine.

The experiments of methane oxychlorination were performed in the flow reactor over the $CuCl_2$-KCl-$LaCl_3$/porous carrier catalyst. The temperature was varied in the range 300–420°C, pressure – 0.1 ÷ 0.9 MPa, the composition of the initial gas was, % vol.: nitrogen – 5–25, methane 25–60, hydrogen chloride – 5–20 oxygen – 2,5–15, the hold up time from 0.1 to 4.5 sec; alumina, inert aluminosilicate, support for catalyst APC (α-Al_2O_3 – 70 %, SiO_2 – 30 %) were used as carriers.

It was found:

- Increasing of temperature leads to the increasing of the reactants conversion and of the yield of deep oxidation products, selectivity of methyl chloride formation is decreased (in the sum of all chloromethanes);

- Increasing of the pressure from 0.1 to 0.9 MPa leads to decreasing of reactants conversion, first of all hydrogen chloride and oxygen by 15–20%, the yield of deep oxidation products is increased as average on 1.5% when other conditions was being constant. The increasing of pressure leads to increasing of the catalyst productivity by target product – methyl chloride – is increased with proportion factor $P^{0.85}$, where P is pressure.

- The ratio of initial reactants effects on the selectivity of methyl chloride formation. Thus, the selectivity of methyl chloride formation is proportional to the HCl and O_2, which were supplied in a stoichiometric ratio of 2:1.

- The decreasing of the hold up time leads to decreasing of the yield of deep oxidation products; also the conversions of the initial reagents, the selectivity of methyl chloride formation is increased.

The best achieved results: selectivity of the chloromethanes (methyl chloride, methylene chloride, chloroform, carbon tetrachloride) formation is 96.3% (the rest are carbon oxides), the part of the target product (methyl chloride) is 92.1% of the sum of chloromethanes, the conversion of oxygen – up to 97.7%, the conversion of hydrogen chloride close to 100%. The hour’s catalyst productivity is 0.66 kg of methyl chloride per 1 l of the catalyst. These results admit to presume that the oxidative chlorination of methane with subsequent pyrolysis of methyl chloride is competitive compared to processes of alkenes preparation from methanol and synthesis gas.

DEVELOPMENT OF EXPERIMENTAL TECHNOLOGIES OF CRUDE OIL HEAVY RESIDUES DEEP PROCESSING WITH THE USE OF RENEWABLE FEEDS

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Currently the products of oil and gas processing are the main source of feed for fuel and chemical industries. At the same time the world energy, which is almost 90% dependent on fossil fuels such as oil, coal and gas, shows clear signs of the crisis due to the rapidly increasing energy consumption in developing countries and is quite really threatened due to global recession in production of traditional light crude oil, the reserves of which in the next 10–15 years will be practically exhausted. By this time, most oil-producing countries, including Russia, will move to production of heavy carboxylic crude oil, however the production technology of such a crude is currently still being developed. Even taking into account the most modern processes of such materials processing, the amount of heavy crude oil residues will increase and new (simple and available) experienced technologies would be required, which would allow to receive from heavy crude oil residues the light oil products in the same volumes as while processing traditional light crude oil.

In the framework of this study for the processing of the future type of heavy hydrocarbon feed it is suggested to use an alternative oil-containing hydrocarbon source of vegetable origin – tall oil. This is large-tonnage product of wood biomass processing at all pulp and paper mills of Russia. It contains fatty acids (C_{18}), resin acids (C_{20}) and unsaponifiables (C_{30}) – natural hydrocarbons and oxygenated compounds (mainly alcohols). Tall oil is a liquid and active product that practically does not freeze at a temperature of minus 30ºC. It mixes easily with model systems of heavy crude oil residues, obtained during crude oil distillation, diluting them. In the future, this mixture of heavy oil residues and renewable hydrocarbon feed undergoes the process of decarboxylation for transition of carboxylic acids into hydrocarbons (C_{17}-C_{19}). The resulting products from this process in regards with composition and properties are coming closest to the traditional petroleum gas oil, which in mixture with the heavy crude oil residues can further be sent to the hydrocracking unit to produce additional quantities of light products modified by the bio-component of natural origin.

CATALYTIC FURFURAL HYDROGENATION

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The climate change, the perspective of finishing oil resource and its rising prices led the world to search for an alternative ways of acquiring valuable chemicals and fuels. In recent years technologies of production the most important chemicals for chemical and automotive industries are developed, especially these which use a renewable source of biomass (biodegradable fraction of products, waste and residues from agriculture, forestry and related industries, as well as the biodegradable fraction of industrial and municipal waste) [1].

However, common availability of biomass (especially the non-food waste type), caused the trend for reduction of dependency from petroleum resources and increased responsibility for the environment. These factors can be the driving forces behind the development of technologies that use derivatives of furfural, which are called, not without a reason, the “sleeping giants”. One might assume that a lot of interest in furan compounds may contribute to the development of new catalytic conversion processes of furfural and its derivatives, which in the future can lower the cost of their production. This could increase the scale of production, which will result in the launch on the market beneficial alternative fuels for spark ignition engines, which are forward-looking replacement for conventional gasoline [2].

This work is devoted to furfural hydrogenation under H_2 over various carbon-supported Pd catalysts. Furfural hydrogenation was carried out on six-cell reactor Multiple Reactor System (MRS) Series 5000 at H_2 a pressure of 6 MPa, at temperatures ranging from 443 to 473°C. To the reactor were added 0.1 g catalyst and 50 ml of pure furfural. The hydrogenation was carried out under continuous stirring (800 rev/min).

Conversion and selectivity of furfuryl alcohol (FA) and of tetrahydrofurfuryl alcohol (THFA), from the reaction time, the furfural hydrogenation using 0.1 g catalyst at temperatures of 453 K, under H_2 pressure of 6 MPa

Catalyst	Conversion, %	Selectivity FA, %	Selectivity THFA, %
2% Pd/activated carbon	5.7	100	-
5% Pd/activated carbon	15.7	87	8
2% Pd/graphite	4.9	83	15
5% Pd/graphite	9.8	9	0.4

The main products were found to be furfuryl and tetrahydrofurfuryl alcohol. The maximum conversion obtained over absorbent carbon 5% Pd (5% Pd/C) catalyst at 453 K and 6 MPa was15.7% with 87% selectivity to furfuryl alcohol (Table). Increasing conversion furfural from 0.68% to 30.5% was observed in the temperature range 443 - 473 K while the formation of furfuryl alcohol and tetrahydrofurfuryl alcohol selectivity decreased from 100 to 84%. Furthermore, it should be noted increasing the temperature above 473 led to rapid furfural polymerization over surface active sites and catalyst deactivation. Thus, the effective hydrogenation catalyst furfural should have a minimal amount of acid-base centers to reduce polymerization processes.

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INTERACTION OF CHEMISTRY AND PHYSICS IN THE PROCESS OF OBTAINING HIGHER ALKYLPHENOLS

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The processes of alkylation of phenols occupy a large place in industrial organic synthesis. Alkylphenols are used to obtain antioxidants, additives for oils and fuels, stabilizers, surfactants and many other things.

In Samara region, higher alkylphenols are used to produce a number of additives for oils and fuels which are in demand among consumers. The effectiveness of the additive depends on the quality of the alkylphenols which also are synthesized in our region using a continuous production technology.

This work is devoted to the problem of homogenization and decomposition of the mixtures. These phenomena are inseparably bound up with the chemical transformations in the process selected. The shift from a homophase to heterophase condition of the system in the reactor is accompanied by a sharp reduction in the speed of reactions and selectivity of the process; the relative role of formation of higher oligomers and alkylphenol ethers increases. The number of them in the end product is tightly regulated. Considering the specifics of the technology of phenol alkylation by higher alkenes, we studied the ‘liquid-liquid’ phase balance in the Phenol+Hexadecene-1 systems in the full range of variation of compositions and Phenol+Hexadecene-1+Water with water content in the phenol practically covering the range used. We determined the form of phase diagrams and the correlation of the critical temperature of the decomposition of the system to the parameters of the process.

The following was established experimentally:

1) the critical temperature of breakdown of the anhydrous binary mixture of Phenol+Hexadecene-1 is equal to 57.8±0.8 oC and corresponds to the correlation Hexadecene/Phenol 0.4±0.5 mole/mole;

2) the shape of the phase diagram depends substantially on the moisture content in the system;

3) the level of the critical temperature for the tri-component mixture Phenol+Hexadecene-Water is substantially higher than for the binary mixture and reaches 100 oC with a correlation of Hexadecene/Phenol equal to 0.264 mole/mole, which corresponds the what is used in production.

To avoid a shift of the system to heterophase condition and, consequently, the worsening of the quality of the intended alkylphenol, it is recommended that you maintain the temperature at the entrance to the reactor at the level of 90–100^{o}C, which is higher than what is used in production.

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ENERGY EFFICIENCY OF COMPLEX COLUMNS FOR THE SEPARATION OF THE BUTANE AND PENTANE PARAFFIN FRACTIONS

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Previously it was shown that the use of distillation sets with the partial thermal coupling is an efficient way to reduce costs for the separation of light hydrocarbons [1]. The efficiency of such schemes has been identified for a project feed composition. However most of gas fractionation plant for any of several reasons are working on raw materials, which composition and properties differ from the design or vary within wide limits. Thereby the question arises about effectiveness predicting for the schemes with thermally coupled heat and material flows at the condition of initial feed composition varying.

The aim of this work is to identify energy consumption of partial thermal coupling distillation systems for the separation of isobutane – n-pentane hydrocarbons fractions with different initial feed compositions and compare them with traditional separation sequences.

Simulation of technological schemes was carried out using licensed software Aspen Hysys ©. SRK model is used for predicting of vapor-liquid equilibrium. The isobutane - n-pentane fraction admixed with propane and n-hexane was considered**.** The purities of products were assigned same for all the schemes and were equal 99.15 and 99.20 mass. % for isobutane and n-butane as the main product fraction components respectively.

The concentration subset of the permissible initial compositions was isolated in the manifold of initial feed composition. It was made by taking in account the balance constraints which deals with the impurities concentrations in the products. Then this concentration subset was divided with sections and secants. As a result, 21 initial feed compositions were obtained in the points of their intersection. Calculation was performed for all those initial compositions for direct and indirect separations, as well as PTCDS [2]. For all schemes parametric optimization was carried out in accordance with [1]. The minimum total heat duties of reboilers were applied as optimization criteria.

Finally it was established that the effectiveness of PTCDS in comparison with traditional distillation sequences varies from 6 to 27% depending on the initial feed composition.

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INCREASING OIL PROCESSING DEPTH BY THE USE OF HYDRODYNAMIC CAVITATION

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Cavitation treatment is used for stimulation of chemical engineering processes taking place in condensed media. Regular studies of influence of hydrodynamic cavitation on petroleum feed are carried out in MITHT named after M.V. Lomonosov. Cavitation condition appears when liquid oil products pass through micro-gap with controlled cross-section under pressure impact. Pressure (several dozens MPa) is generated by piston pump in desintegrator DA-1. The purpose of research is increasing processing depth of petroleum feed.

So far were used model mixtures of alkanes C_{13}-C_{15}, C_{13}-C_{17}, C_{21}-C_{38}, a number of samples of stock oil originated from different fields, straight-run fuel oil and hydrotreated vacuum gas oil as objects of research. Findings gave opportunity to reveal a set of regularities putting together physical and chemical properties of feedstock and conditions of cavitation treatment with fractional and hydrocarbon composition of obtained products.

Particularly, it has been determined that the most effect (increase of importance of destructive changes and increase in yield of distillates with boiling point up to 500°C) of primary processing is achieved by preliminary cavitation treatment of high-wax oil containing mainly medium-chain n-alkanes C_{21+}. By contrast, increase of total content of silica-gel tars and asphaltenes in oil for more than 14–18% is associated with prevalence of condensing changes and increase in yield of heavy residue – asphalt.

It has been showed that multi-cycle cavitation treatment of oil and fuel oil allows, in comparison with one-cycle treatment, to increase cracking effect during following distillation, i.e. increase feed processing depth. However this effect is not result of multiplying treatment effect of one cycle on amount of cycles. The optimal amount of cycles and cavitation efficiency depends on feed nature. Two-three cycles of preliminary cavitation treatment are enough to reach maximum yield of distillate fractions during oil distillation. However achievement of the same effect for fuel oil requires eight-ten treatment cycles.

The opportunity to increase efficiency of catalytic cracking of hydrotreated vacuum gas oil by its activation under hydrodynamic cavitation has been revealed (together with INHS n.a. A.V. Topchiev). Microspheric zeolite-containing catalyst was used for cracking (temperature 500°C, feed mass flow 7 h^{-1}). After cavitation treatment (one cycle with $P = 40$ MPa) yield of gasoline fraction (C_5-200°C) increased for 14% rel.; yield of heavy gas oil decreased for 27% rel. and yield of coke – for 13.6% rel. Increase in yield of gaseous products for 8.6% rel. is accompanied by increase in propylene yield for 13.9% rel.

The results have been obtained within the framework of State task of the Ministry of Education and Science of the Russian Federation.

3-CARENE ISOMERIZATION OVER MODIFIED GLAUCONITE

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Isomerization of 3-carene in the presence of acid catalysts yields 2-carene and a mixture of mentadienes as intermediate products. The last in turn undergoes disproportionation to obtain *p*-cymene as a final product [1], which is applied in the production of fragrance compounds (carvacrol, musk and thymol) [2].

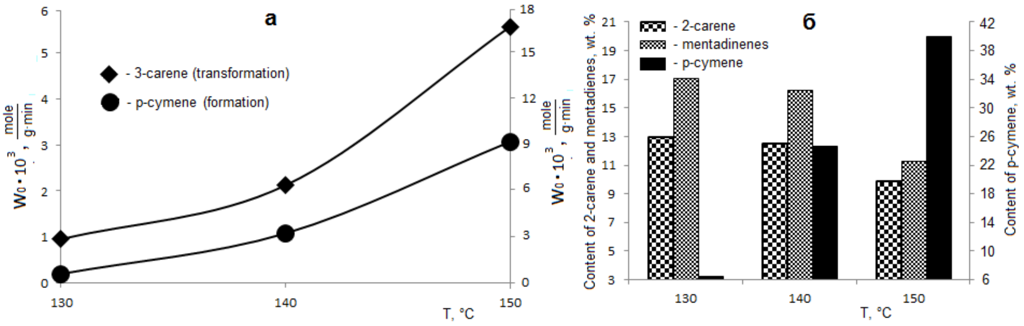
The process of isomerization of 3-carene (Acrors Organics, Belgium, 96%) was carried out in the presence of 1,0 wt. % of glauconite. Catalyst was treated with 50 ml/g of 10% HCl at 30, 50, 70 and 90°C.

Glauconite	Content of oxides, %							Specific surface, m^2/g
	Al_2O_3	SiO_2	FeO	MgO	K_2O	CaO	TiO_2	
Initial	11,6	58,3	20,8	3,6	4,6	0,5	0,5	29,0
Treated by HCl at T, °C: 30	11,5	58,9	20,5	3,5	4,6	0,5	0,5	53,0
50	11,4	59,6	20,1	3,4	4,5	0,5	0,5	65,0
70	10,8	61,7	19,1	3,1	4,4	0,4	0,5	77,0
90	7,8	72,7	13,7	2,1	2,8	0,3	0,4	162,0

The activation of gauconite accounted for reduction of Al_2O_3, FeO, MgO, K_2O and CaO in its composition and amount of removal cations increased with the activation temperature rise. The specific surface of glauconite grew and the maximize value of which was observed when the treatment temperature was 90°C (the table).

3-Carene conversion was 50,8 and 87,7% for 6 h in the presence of samples modified at 30 and 90 °C while amount of p-cymene in isomerizate was 9,2 and 36,4 wt. %, content of 2-carene was 14,1 and 10,4 wt. % and amount of mentadienes was 16,2 and 13,3 wt. % respectively.

The influence of reaction temperature on the rate of 3-carene transformation and *p*-cymene formation was studied at 130, 140 and 150°C in the presence of 1 wt. % of glauconite activated with 10% HCl at 90 °C. It was established that the initial rate of 3-carene transformation was $2{,}9 \cdot 10^{-3}$ mole/g·min at 130 °C and it raised up to $16{,}7 \cdot 10^{-3}$ mole/g·min with increasing process temperature to 150 °C. Meanwhile *p*-cymene formation rate raised from $0{,}2 \cdot 10^{-3}$ to $3{,}1 \cdot 10^{-3}$ mole/g·min (fig. a).



It was shown that content of 2-carene and mentadienes in isomerizate was 13,0 and 17,1 wt. % for 3 h and amount of them decreased down to 9,9 and 11,3 wt. % with increasing of reaction temperature to 150°C. Meanwhile content of *p*-cymene in the mixture raised from 6,4 to 39,9 wt. %.

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DICYCLOPENTENE EPOXIDE SYNTHESIS WITH USING OXIDIZERS OF VARIOUS NATURE

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The original direction of use dicyclopentadiene for the purpose of receiving a number of oxygen-containing derivatives is offered and is developed. The first stage of this direction are hydrogenation dicyclopentadiene in dicyclopentene. This stage define efficiency of the direction as a whole, and dicyclopentene epoxide are key compound of this direction [1, 2].

Oxidation of olefins by organic hydroperoxides is effective method of receiving epoxides. For preparation dicyclopentene epoxide with a high yield is necessary ratio cycloolefine : hydroperoxide as 3:1. This condition doesn't depend on structure of cycloolefine and requires process of products rectification of this reaction. However, the separation of the products epoxidation of dicyclopentadiene complicate the fact that dicyclopenten and its epoxide are solids.

In this regard our attention was paid to alternative methods of preparation dicyclopentene epoxide, first of all, to a method of oxidation of olefins by peracids. The wide range peracids are oxidizing agents and process of oxidation doesn't demand of using surplus cycloolefine and oxidation catalysts. It is shown that use of peracetic acid in process of oxidation dicyclopentene is accompanied by high quantitative results. The composition of products of oxidation is rather simple and epoxide is result of crystallization from solution.

For receiving epoxides of cycloolefines can be used water solution of hydrogen peroxide. Process of oxidation in this case proceeds in heterophase liquids system. As oxidation catalysts dicyclopentene are offered tungstate and phosphorustungstate of sodium as anions of these salts form rather stable peroxianions. They carry out a role of a carrier of active oxygen to the oxidizing bond of molecule. Dependence of an exit of a target product from concentration of the catalyst has difficult character, and certain value pH of solution for preparation dicyclopentene epoxide with a high yield are necessary. High result of synthesis of dicyclopentene epoxide requires the dosed supply of water solution of hydrogen peroxide. As result, process of oxidation by water solution of hydrogen peroxide is rather difficult for realization in practice because he heterogeneous, periodic, has high duration of oxidation and depends on many factors.

The simplest method of receiving epoxides this the method of direct oxidation of olefins by molecular oxygen. Among cycloolefines it is applicable only for cyclooctene [3]. We have shown that use of a range of catalytic systems in the course of oxidation cyclooctene allows to increase process speed at rather low temperature of oxidation and to receive target epoxide at practical lack of carbonyl compounds in reaction products.

Thus, for receiving dicyclopentene epoxide we offer to use its oxidation by peracides. The received results are important for the organization of processes of receiving oxygen-containing derivatives dicyclopentene which are based on modern energy-saving and resource-saving technology

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THE DEVELOPMENT OF *para-TERT*-BUTYLPHENOL PRODUCING PROCESS

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The field of using of *para*-*tert*-butylphenol (*p*-TBP) widen constantly: if it was applied, in general, in paint and varnish industry earlier, then now – in medical targets, in tire industry, in catalytic matrix production. Changing of special purpose leads to necessity of development of its producing process to improve quality. The development method chosen by us is connected with transfer to another catalytic system. That helps to employ the source, given with thermodynamic of process, like fullest.

Since 1986 in the industry process of *p*-TBP production by alkylation of phenol with isobutene, realized on CJSC «NNK» (Novokuibyshevsk), macroporous sulfur cation-exchange resin KU-23 was applied. But now there is a large range of sulfur cation exchangers, possessing by manufacturer's data, with improved catalytic and mechanical features. The kinetic experimental results were the comparison criterion of cation exchanger efficiency.

For these purposes it was studied the kinetic of transalkylation, proceeding in the system «phenol-*tert*-butylphenol» in the presence of cation exchangers KU-23, Amberlyst 36 Dry and Tulsion T-66 MP. For Amberlyst 36 Dry и Tulsion T-66 MP investigation was carried out in mixture reactor with static method. Process isothermality was providing with thermostating of heat-transfer agents, feeding in heating jacket, and permanent stirring of reaction mass. Such data was taken from literature for KU-23.

It was found on the basis of experimental data:

- equilibrium of system is reached faster in the presence of Amberlyst 36 Dry in temperature range 353–403 K;

- value of pre-exponential factor of proceeding reaction in the presence of Amberlyst 36 Dry excels KU-23 and Tulsion T-66 MP in similar parameter.

- thermodynamic characteristics were calculated on the basis of experimental and literature data for reaction, describing equilibrium in the system.

Differences in physical-chemical features of Amberlyst 36 Dry from other catalysts are higher rate of static exchange capacity, mechanical and thermal stability, lesser specific pore size and moisture content in commodity form.

Therefore substitution of KU-23 for more active Amberlyst 36 Dry allows to increase the yield of target product from the unit of reaction space volume, prolong catalyst life, extend temperature range of the process specifically reduced the initial temperature of alkylation, decrease consumption of flushing phenol under cation exchanger pretreatment before operation.

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LIQUID PHASE ALKYLATION OF BENZENE WITH (C_3-C_4) ALKENES

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At present, industrial alkylation of aromatic hydrocarbons with lower alkenes is carried out generally in a liquid-gas, or in gas phase.

Alkylation in the liquid-gas is carried out on the catalyst complex based on $AlCl_3$. The main advantage of this process is that the composition of the reaction mixture is close to chemical equilibrium. This allows to obtain a high concentration maximum of mono-alkylaromatic compound. The disadvantage of this process is a complicated and multi-stage procedure of the reaction mass treatment.

Gas-phase alkylation is carried out on various heterogeneous catalysts (zeolites of various modifications, phosphoric acid on the support). The main advantage of this process is the ease treatment of the reaction mass. The disadvantage of this process is a large excess of an aromatic hydrocarbon in relation to alkene in raw materials and the short catalyst lifetime.

With the switch to the liquid-phase technologies, intensity of processes should appreciably increase, even at moderate temperatures. Realization low-temperature liquid-phase of the technology requires the availability of affordable and highly selective catalysts, which provide a stable process performance during prolonged their lifetime. As such catalysts have been analyze the possibilities of modern polymer based catalysts polymeric sulfonic acid (Sulfo-kationit).

On the basis of the experiment we have established the basic laws of the alkylation of benzene with propylene to obtain isopropylbenzene and alkylation of benzene with normal butenes to obtain sec-butylbenzene on modern Sulfo-kationit. It is found that the alkylation of benzene with alkenes on a Sulfo-kationit is a high-speed and highly-selective process. Determine the necessary contact time at which the almost complete conversion of alkenes at different temperatures alkylation of benzene with propylene and linear butenes. It is established that, after to convert the whole alkene composition of the reaction mass does not change, that is, mutual conversion of alkylbenzenes not occur.

Also found that the liquid-phase alkylation of aromatic hydrocarbons with low alkenes on modern Sulfo-kationit is obtain high maximum concentration of mono-alkylbenzene, which is close to chemical equilibrium, analogously to alkylated in system of liquid-gas on $AlCl_3$. At the same ease of treatment of the reaction mass is the same as in the gas-phase process.

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THE RESEARCH RESULTS OF INDIVIDUAL HYDROCARBONS AND COMMERCIAL GASOLINE DEPOSITION TENDENCY IN INJECTORS

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Currently, the bulk of the spark-ignition engines are fitted with the fuel injection system. Thus, nozzles contamination is the main factor, which causes injection system degradation of the modern gasoline engines under running conditions.

Two methods are regulated in WWFC to assess contamination of fuel injection nozzles: motor bench ASTMD 6421[1] (10,000 miles) and running ASTM D5598 [2]. Both of these methods are difficult to realize and expensive.

The method has been developed and implemented on OSV-1 [3] device in FAE «The 25th State Research Institute of Chemmotology of the Russian Ministry of Defence» on the basis of regularities analysis of deposits formation on gasoline engines injectors. Deposition tendency index of gasoline is scoring visual estimation of nozzle bottom optical density (darkening). Based on the researches, this index has the range, which is sufficient for commercial gasoline differentiation.

Individual hydrocarbons (typical for gasoline) and their mixtures were tested for the determination of the chemical composition, which causes deposits formation. It is specified that unsaturated hydrocarbons and nitrogen compounds deeply influence on deposits formation. Besides, deposits formation process is of nontrivial nature, because there is neither additive effect nor synergistic one.

More than that, 45 commercial gasoline samples of different grades and manufactures were tested on the device. The frequency diagram was made on the basis of tests results. It revealed three distinct peaks. The first one (from 0 to 1,5 points)corresponds to the gasoline, which has detergent as a part. The second peak corresponds to the most mass product of representative hydrocarbon composition without any detergents (from 2 to 5 points). The last peak is obtained during gasoline tests; in this case the gasoline contains MMA and a considerable amount of catalytic cracking products and it doesn’t contain any detergents. Moreover, one tested sample, containing catalytic cracking products, led to stop needle injector “hanging” and it isn’t considered in statistics.

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3. Method for estimating of automobile gasoline to form deposits in the injectors on OSV-1 device. Abstracts of the V International extramural scientific conference of young scientists "Actual problems of science and technology–2012", Ufa, 22-24 November 2012. – Ufa: Oil and Gas Business, 2012. Vol.1. – p.180–182.

CONSISTENT PATTERNS OF 2,4-DINITROANILINE ACYLATION BY 4-NITROBENZOYL CHLORIDE IN THE PRESENSE OF IRON (III) CHLORIDE

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2',4'4-Trinitrobenzanilide (TNBA) – an intermediate product for synthesis of 5(6)-amino-2-(4-aminophenyl)benzimidazole – is prepared by acylation of 2,4-dinitroaniline (DNA) with 4-nitrobenzoyl chloride (NBC) in chlorobenzene in the presence of iron (III) chloride as a catalyst. The resulting TNBA inhibits the process of acylation as a result of complexation with $FeCl_3$ [1].

Along with the main reaction NBC is also consumed in the side reaction resulting in the formation of anhydride reacted with 4-nitrobenzoic acid (NBA), present in the feedstock due to hydrolysis of 4-nitrobenzoyl chloride. It is found that the generation of anhydride of 4-nitrobenzoic acid (ANBA) is also catalyzed by iron (III) chloride, where, as in the acylation reaction of the DNA, there is also manifested an effect of inhibiting by the reaction product.

The stability constant of the complex of $FeCl_3$ with ANBA is higher than its complexes with NBC and TNBA 57 and 7 times, respectively.

Catalyzed by iron (III) chloride acylation of NBA with 4-nitrobenzoyl chloride is the first order on catalyst and on NBA and is characterized by high initial velocity, which then drops sharply as a result of binding of the catalyst.

It has been established that the reaction of ANBA formation can also proceed in non-catalytic route. Non-catalytic reaction is the second general order. The reaction velocity constants and the activation energy have been determined. However, the initial velocity of the non-catalytic reaction is two orders lower than the catalytic one.

Derived and experimentally validated has been the kinetic model of acylation reaction of DNA with 4-nitrobenzoyl chloride, taking into account all possible effects of complexation with iron (III) chloride.

The kinetics of TNBA building-up process is described by a system of two equations for TNBA and ANBA formation rate, taking into account the effects of complexation of the catalyst with the products of both reactions.

The model obtained has been used to calculate the reactor unit, select the modes and control the process.

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INVESTIGATION OF THE COMPOSITION AND PROPERTIES OF SULFATES OF AROMATIC DI- AND TRIAMINES

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Aromatic amines such as p-phenylenediamine (PPDA), 2-chloro-1,4-phenylenediamine (Cl-PPDA), 2'-chloro-4,4'-diaminobenzanilide (DACBA), 5(6)-amino-2-(4-aminophenyl)benzimidazole (DAPBI), 2',4,4'-triaminobenzanilid (TABA) are used as monomers and intermediates for their synthesis. Amines having two amino groups in a single core are easily oxidized. Their precipitation out the reaction solutions as sulfates enables to obtain stable compounds.

It has been established that all the specified amines when being treated with sulfuric acid produce monosulfates.

The literature describes a study of sulphate PPD by X-ray diffraction method (XRD). Its structure features the involvement of all available hydrogen atoms in the formation of hydrogen bonds with the oxygen atoms of sulfuric acid. The XRD of monosulfates of a wide range of amines showed that this property is characteristic of other salts of di-and triamines (Figures 1 and 2) and, obviously, is the cause of their low solubility both in water and in organic solvents.

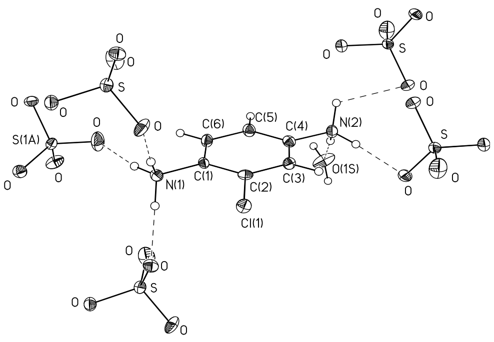

Fig. 1. Environment of cationic fragment formed by hydrogen bonding in a crystal of sulphate of 2'-chloro-4,4'-diaminobenzanilide.

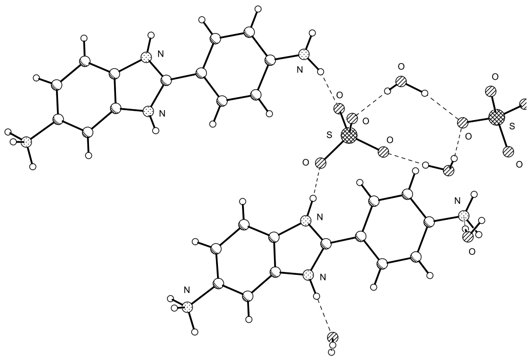

Fig. 2. Scheme of associate $DAPBI \cdot H_2SO_4 \cdot 2H_2O$.

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THEORETICAL FOUNDATIONS OF REACTION OF HOMOGENEOUSLY CATALYTIC VINYLATION OF AROMATIC ACETYLENE ALCOHOLS

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Vinylation reaction of aromatic acetylene alcohols (AAA) containing phenyl group in its molecule in the presence of acetylene has been investigated and properly vinyl ethers (VE) have been synthesized.

The influence of temperature, catalyst and solutions nature on the yield of AAA VE has been studied systematically and analyzed. On the basis of received results DMSO solution in the presence of catalyst KOH, when acetylene influences on AAA at temperature 120°C, for 6 hours it has been determined that VE comes out with highest yield.

We can clarify the influence of temperature, catalyst and solutions nature on the AAA VE yield as following: It has been determined that VE comes out with maximum yield when catalyst KOH, which with higher base among the used catalysts, is used. During the process at first AAA: having interacted 1-phenyl-3-methylpentin-1-ol-3 (I), 1-phenyl-3,4-dimethyl-pentyn-1-ol-3 (II), 1-phenyl-3,4,4-trimethylpentyn-1-ol-3 (III) and 1,3-diphenylbutyn-1-ol-3 (IV) with alkalis, interval compounds changes into alcoholates and accompanying with acetylene VE is yielded. Herein, because of potassium alcoholate's activity being higher than lithium and sodium alcoholates. During this reaction it has been determined the yield of product is higher because of having higher catalytic activity potassium alcoholate than lithium and sodium alcoholates.

At selected temperatures (80–140°C) product is synthesized with higher yield at temperature 120°C. Orientation polarity of hydrogen positive charged in AAA hydroxyl group towards triple bond of acetylene depends on the exchanging of catalysts metal cations with active hydrogen of acetylene and acetylenides forming.

It can be explained the coming out of AAA VE with higher yield in the presence of DMFA than DMSO. DMFA is considered as a solution in average solidity. Positive charge in the nitrogen atom allows DMFA reacting as a weak proton acid. Owing to the presence of autoprotolysis in DMFA, it can't create convenient homogeneous medium for the process of reaction, as a result product is synthesized with partly low yield. And DMSO possesses two nucleophil consisting of solid-oxygen and soft sulphur atoms. Because of relatively strong protonation of hydrogen atoms in it, having been drawn with the help of alkalis, catalytic active interval complexes are formed. It causes the rise of product yield, at the same time creating convenient medium for the acetylene connection. It has been observed the decrease in the product yield on account of the increase of the number of carbon atoms or the increase of radicals branching in the main chain of AAA molecule and obstacle spacial them to compound with acetylene. Also, the number of carbon atoms in the main change are equal (II and III), but the formation of VE goes worse with radicals branching (ethyl, isopropyl and tertiary butyl). Besides, it has been observed the product yield will be maximum on account of drawing more electron butyls of phenyl radicals in the presence of 1,3-diphenylbutin-1-ol-3 containing two aromatic nucleus. The cause of this is that the electronegativeness of phenyl group is higher than the electronegativeness of ethyl, isopropyl and tertiary butyl. In the hydroxyl oxygen negative charge falls down, acidity of alcohol goes up; as a result alcoholate is formed with higher yield. Formation of alcoholates with more high yield causes being convenient medium for acetylene joining. And it may synthesize the product with higher yield.

DEVELOPMENT OF CHLOROPARAFFIN OXIDATION METHOD IN ORDER TO OBTAIN MULTIFUNCTIONAL ADDITIVES FOR PVC PROCESSING

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Chloroparaffins are industrial products produced in Volgograd region. They mainly used as secondary plasticizers for polyvinylchloride (PVC) processing and give to the goods next useful properties: low cost, low combustibility, high shock resistance etc. But their compatibility with PVC is insufficient and so plasticizing effect is. Therefore, chloroparaffins are used jointly with primary plasticizers (phthalate plasticizers in particular). Chloroparaffin content is no more than 30 weight % in plasticizing system. Use of phthalate plasticizer raises the toxicity and cost of PVC goods. Therefore, expansion of the range of additives based on chloroparaffins is an actual problem and the subject of the research.

As far as most primary plasticizers are esters, it is necessary to modify chloroparaffins in order to place etheric or carboxylic group into chloroparaffin. The most available and cheap oxidant is air. It has been established that chloroparaffins are not oxidized without catalysis of variable valence metals. It has been shown that oxidation of chloroparaffin can be carried out in the presence of manganese salts [1] similarly to paraffin oxidation. Our investigations showed that cobalt stearate is more effective catalyst than manganese one [2].

Chloroparaffin oxidation with air in the presence of cobalt stearate enables us to obtain mixture of higher chlorinated esters (which provide primary plasticizer effect of the composition), unreacted chloroparaffin (secondary plasticizer) and higher chlorinated acids. It has been established that maximum concentration of acids and esters can be obtained in the presence of 8,5 weight % of cobalt stearate. Molar ratio acids: esters is 2:1 after 20 hours of oxidation.

Adding to the cobalt stearate equimolar quantity of potassium stearate gave us the opportunity to decrease the concentration of stearate cobalt in 1,5 times and obtain the oxidate of better quality.

In order of further improving plasticizing properties the mixture of oxidation products obtained (so called oxidate) has been put into etherification with ethyl and octyl alcohols. Obtained ethyl and octyl esters of higher chlorinated acids in the medium of other oxidate components are effective plasticizing additive for PVC and composition with octyl ester form dry mixture in 25% faster than ethyl ester containing one. Plasticizing effect of the additives has been estimated as the time of plasticizer absorption by PVC to dry mixture formation.

The other way of making additive for PVC is to get salts of higher chlorinated acids, which has a stabilizing effect on PVC and industrial chloroparaffins. As far as calcium stearate is widely used stabilizer for PVC, suspension of calcium salts of higher chlorinated acids has been obtained as a result of neutralization of acids by calcium hydroxide in the oxidate medium. In order to estimate stabilizing effect of new additive calcium stearate suspension in the chloroparaffin medium has been made. Test of new stabilizing additive carried out on chloroparaffins because of the similar mechanism of destruction PVC and chloroparaffins. Test has shown that new multifunctional additive is twice more thermostable that corresponding calcium stearate.

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Section 3

Chemistry and Technology of Medical Products and Biologically Active Compounds

DETERMINATION OF CONTENT OF CHLOROGENIC ACID IN FRUITS OF THE BARBERRY IN DAGHESTAN POPULATIONS

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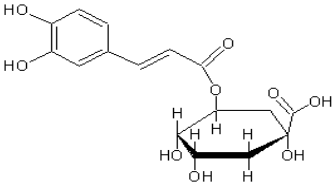
Vitamins and minerals are particularly important to ensure the normal human life. They are in an easily digestible form and optimal ration for the human organism in fruits and berries.

Barberry is one of these high-value crops with rich biochemical composition and grows in the Caucasus, especially in Dagestan.

Fruit of barberry have a complex chemical composition. They contain vitamins, organic acids, carbohydrates, minerals, alkaloids, most of which is berberine [1], which stimulates bile secretion, lowers arterial pressure, increases rhythm and amplitude of heart contractions. Berberine has also styptic and antimicrobial action.

The main component of phenolic groups in the fruit of barberry is chlorogenic acid $C_{16}H_{18}O_9$:



Interest in chlorogenic acid is not accidental. The method of radioactive tracers demonstrated that the substituted cinnamic acids, which are found in plants primarily in the form of esters, are intermediates in the synthesis of lignin amino acids (phenylalanine and tyrosine.) There is some research in which chlorogenic acid is regarded as a growth regulator, as a protective factor against some microorganisms [2]. Its content correlates with the antioxidant activity of coffee.

But nevertheless there is a lack of information about the biochemical role of chlorogenic acid in plants. Therefore researches of determination of the chlorogenic acid in plants remain relevant. The existence of chlorogenic acid in fruits of the barberry is mentioned in [3].

We investigated the content of chlorogenic acid in the fruit of barberry, which was subjected to chromatography extract of barberry.

Studies have shown that the content of chlorogenic acid in the fruit of barberry reaches 4%, which is the reason for the high antioxidant activity of barberry fruit and infusions based on them.

1. http://www.mag.org.ua
2. Rubin B.A., Artsikhovskaya E.B. Biochemistry and physiology of plants immunity. Moscow, 1968.
3. Vereskovsky V.V., Shapiro D.K., Flavonoids, phenolic acids and oksikumarina of different fruit species of the genus Berberis // Chemistry of Natural Compounds. 1986. № 4. P. 512–513.

SYNTHESIS OF 1-BUTYL-3,6-DIAZAHOMOADAMANTAN-9-ONE

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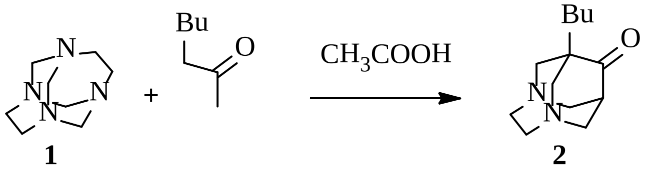
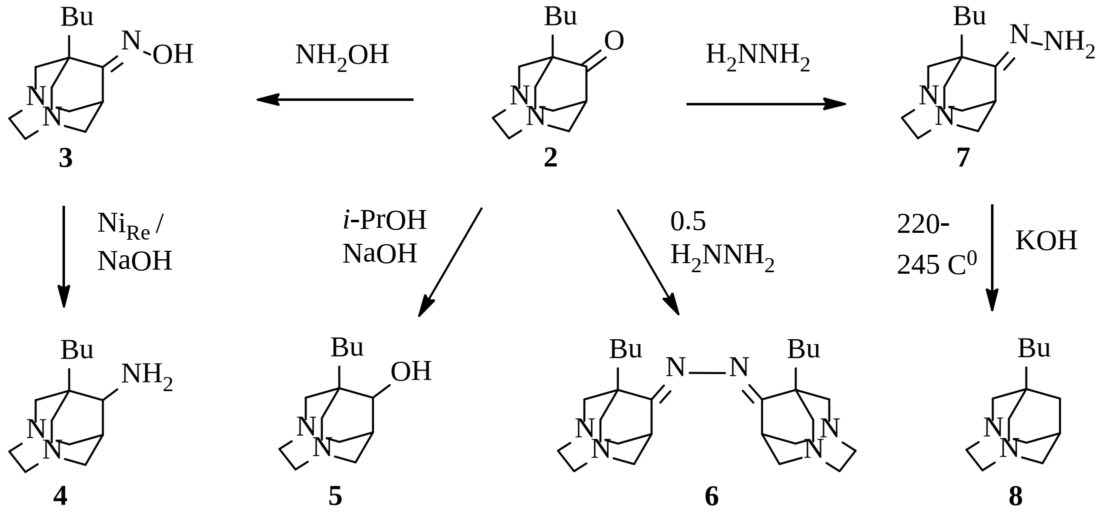
In our earlier work [1], we developed different methods of synthesizing 3,6-diazahomoadamantane. In this work, the 1-butyl-3,6-diazahomoadamantan-9-one **2** was synthesized by condensation of 2-heptanone with 1,3,6,8- tetraazatricyclo-[4.4.1.1^{3,8}]dodecane **1**.



By reacting ketone **2** with hydroxylamine, 1-butyl-3,6-diazahomoadamantan-9-one oxime was obtained. Then oxime **3** was reduced using Ni-Al alloy (Raney alloy) in awater-alkaline medium into 1-butyl-3,6-diazahomoadamantan-9-amine **4**. By heating ketone **2** with NaOH in isopropyl alcohol, 1-butyl-3,6-diazahomoadamantan-9-ol **5** was synthesized. Ketone 2 was reduced by the Wolff-Kishner reaction via hydrazone **7** into 1-butyl-3,6-diazahomo-adamantane **8**. By heating of ketone **2** with hydrazine, azine **6** was obtained. The structure of the compounds (**1-8**) was verified by IR-, ^{1}H-NMR-spectroscopy and by mass spectrometry.



1. A.I. Kuznetsov, I.M. Senan, R.T. Alasadi, A.H. Shukkur, T.M. Serova // *Russian J. Org. Chem.* **2013**, *49*, 1670.

HIGHER FUNGI – PERSPECTIVE RAW MATERIALS FOR THE SYNTHESIS OF BIOLOGICALLY ACTIVE SUBSTANCES

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At present, one of the important problems is a rational use of natural resources. Among diverse organisms, higher fungi are a major source of biologically active natural products. Fungal polysaccharides attract a lot of attention due to their multiple biological properties. The insoluble part of the cell wall of musrooms is a complex of three biopolymers mainly, chitin, glucans and melanin, each of which itself is of a great practical value. Native higher fungi are of interest from the viewpoint of medicinal chemistry and offer valuable raw materials for the synthesis of biologically active substances. Therefore, the isolation, identification, and study of the physicochemical and sorption properties of these natural biopolymers represent a priory field in the investigation of natural compounds.

We report the develop scheme for the isolation chitin-glucan and chitin-glucan-melanin complexes from various kind of native biomass of fungi belonging to classes *Basidiomycetes* and *Ascomycetes*, and the study their physicochemical and sorption properties.

A four-stage procedure for the isolation chitin-containing complexes included deproteinization (2% NaOH + 0.1% sodium stearate, 83–85^{o}C, 2 h), demineralization (1% HCl, 55–60^{o}C, 2h), depigmentaion (5% H_2O_2 in ammonia (30–35^{o}C, 4 h)), and deglucanization (2% NaOH, 83–85^{o}C, 2 h). Variations occurring in the semiproduct composition (the content of water, mineral and organic substances, total nitrogen, and D-glucosamine) during the processing were monitoring. The original raw material and the chitin-containing materials were characterized on the basis of results of Fourier transform infrared spectroscopy, X-ray analysis, and pyrolytic gas chromatography using crustacean chitin as reference compound. The content of chitin in the final products was 70% for *A.mellea* and 50% for *M.esculenta*. The possibility of obtaining chitin-containing materials with the required properties by selecting the fungal species and treatment conditions (the succession and repetition of certain stages) is demonstrated.

The result obtained that all investigated samples have the structure of α-chitin. However depending on a kind and, especially from a class of a mushroom biomass, final samples have the different ratios of component chains (chitin-glucan-melanin), and in some cases can contain segmental chitosan units. This defines the structural heterogeneity and a degree of orderliness of a material, and also hydrogen bond behavior and macromolecule packing.

We report the sorption characteristics isolated biopolymrs in relation to water and ions of heavy metals (Pb^{2+}, Ni^{2+} and Cd^{2+}). The maximal adsorption capacity of biopolymers is reached in 40-60 minutes and changes in the following order: Pb^{2+} (0,8–1,0 г/г) > Cd^{2+} (0,5–0,87 г/г) > Ni^{2+} (0,2–0,3 г/г). In case of Pb^{2+} and Cd^{2+} the adsorption capacity of polymer depends on the scheme of processing of a fungal biomass and type of a mushroom. It is found that adsorption mechanisms of Pb^{2+} and Cd^{2+} and ions Ni^{2+} are various. We proposed possible mechanisms of the metal adsorption on the investigated biopolymers.

SYNTHESIS AND CHEMICAL TRANSFORMATION
OF 2-R-6-R$_1$-IMIDAZO-[2,1-B]-1,3,4-THIADIASOLE

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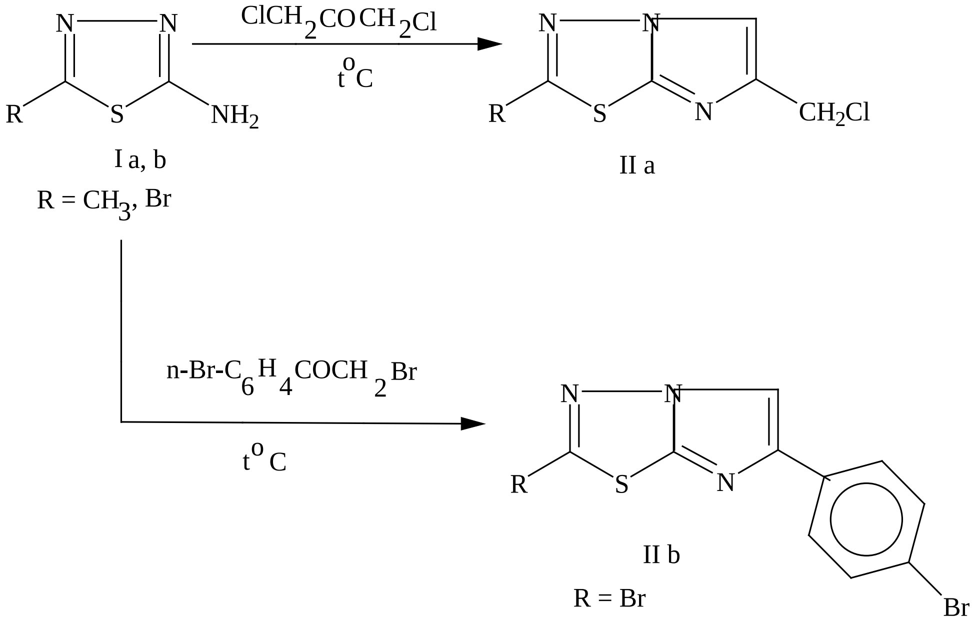
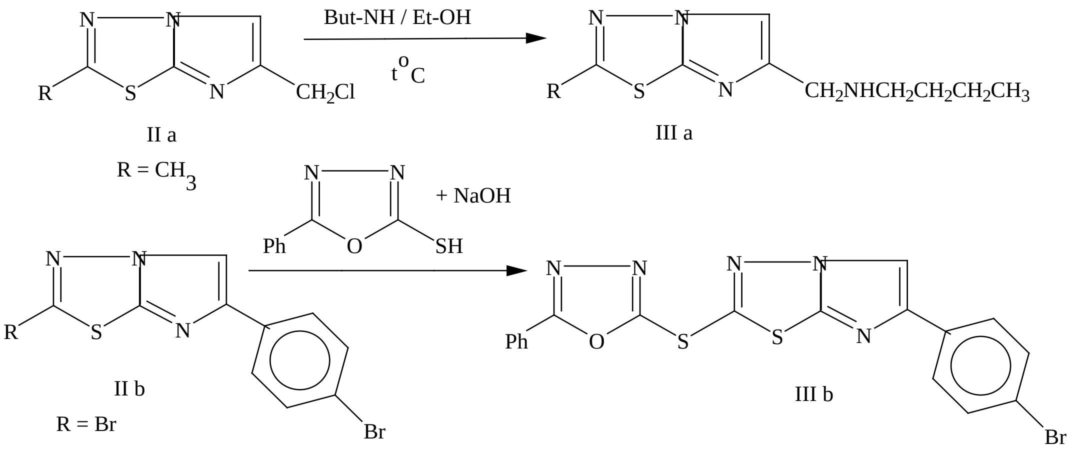
In search of the biologically active compounds we obtained a new modifying series of derivatives of imidazothiadiazoles – 2-methyl-6-chloromethylene- and 2-bromo-6-N-bromphenylimidazo-[2,1-b]-1,3,4-thiadiazole by cyclization of 2-R-5-amino-1,3,4-thiadiazole (where R = CH_3, Br) with 1,3-dichloracetone and *p*-bromphenylacetylbromide.



The reaction of condensation of 2-R-5-amino-1,3,4-thiadiazole (Ia, b) with 1,3-dichloroacetone, and *p*-bromo-phenacylbromide produces imidazo-[2,1-b]-1b3b4- thiadiazole systems (IIa, b).

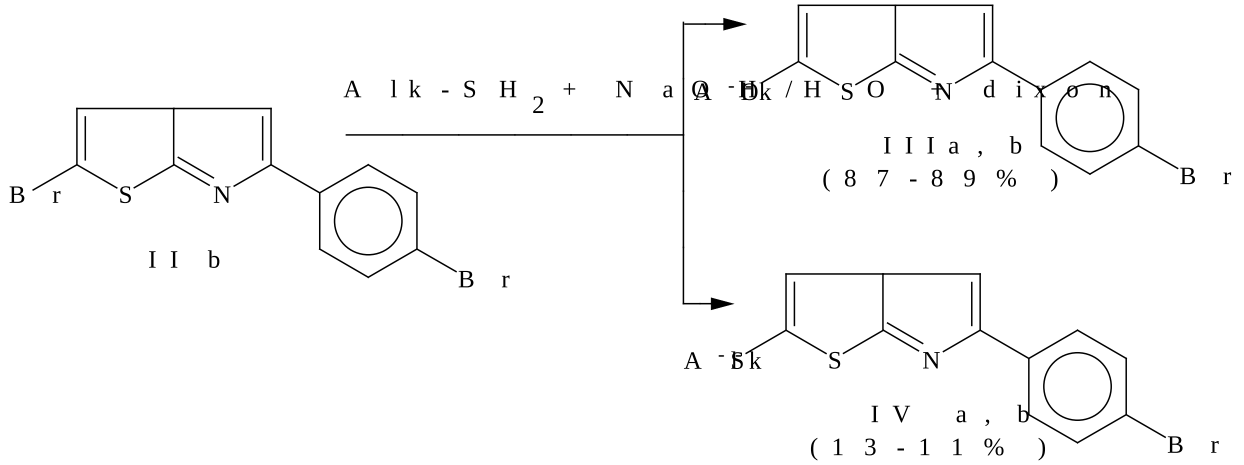
To determine the reactivity of the halogen's atom in the II a, b , we have studied the reaction of compounds II a, b with different nucleophilic agents, including butylamine, 2-phenyl-5-thio-1,3,4-oxadiazole and alkylthiol.



The reaction of compound II with buthylamine was proceeded at the reflux temperature of the solvent.

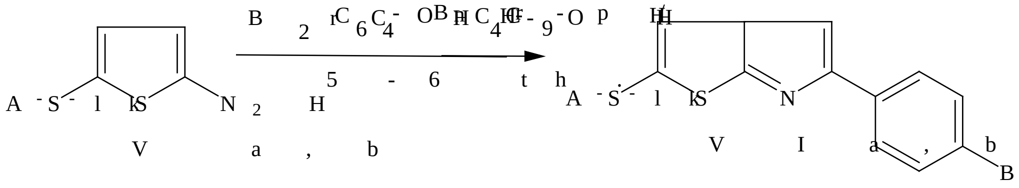
A nucleophilic substitution reaction the compound II b with 2-phenyl-5-thio-1,3,4-oxadiazole was proceeded in a solution of ethanol – DMF at room temperature and allowed to obtain the corresponding desired product (III b) in good yield.

When attempting reacting II b with sodium thiolate's salts of aliphatic compounds in water-dioxane, at room temperature with a target product is produced 2-alkoxy-6-*p*-bromphenylimidazo-[2,1-b]-1,3,4-thiadiazole (III a, b). Using ^{1}H- ,^{13}C- NMR and mass spectra of these compounds we studied the structure and we found that compound III a, b correspond to the following structures with molecular weights 310.2 and 324.2 :



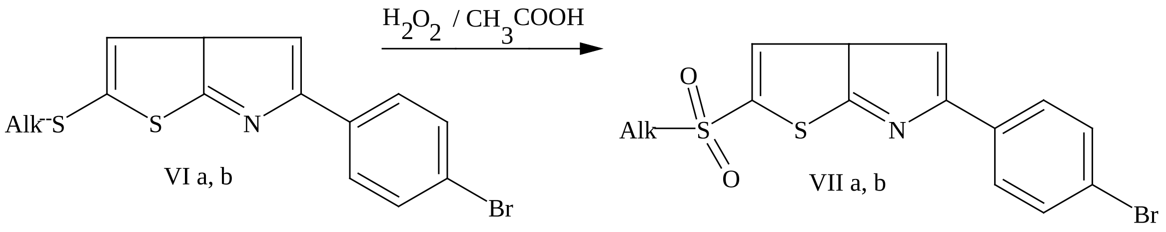
Alk = CH_3, C_2H_5

However, for resolve this problem have been studied reaction of cyclization of 2-alkylthio-5-amino-1,3,4-thiadiazoles (V) with *p*-bromacetylbromide in butanol with heating medium for 5-6 hrs. In result we obtained 2-alkylthio-6-*p*-bromphenylimidazo-[2,1-b]-1,3,4-thiadiazole (VI a, b) with a yield of 68-72 %.



Alk = CH_3, C_2H_5

Also we studied the reaction of oxidation VI a, b with hydrogen peroxide in glacial acetic acid to give the corresponding 2-alkylsulfoxide-6-*p*-bromphenylimidazo-[2,1-b]-1,3,4-thiadiazole.



The structure of the obtained compounds was installed by ^{1}H-, ^{13}C-NMR, and IR-spectroscopy.

METHOD FOR INCREASE AND SYNCHRONIZATION OF HATCHING OF CHICKS BY MEANS OF IODINATED NUTRITIENTS *IN OVO*

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Industry-wide increase of hatching of chicks even by 1–2 % makes it possible to additionally get tens of millions of birds. Therefore, new highly biologically active preparations are searched for on a constant basis.

In this regard, the study of influence of preparations which contain iodine is of particular scientific interest. It is known that this particular element is actively included in thyroid hormones, according to the data of Nobikuni et al., (1989), which are largely responsible for the processes of hatching and synchronization of mass hatching of chicks. It should be noted that these hormones display antioxidant activity which is expressed in regulation of intensiveness of lipid peroxidation. This feature is very important for hen embryos due to the hazard of impact of many stressors to developing organisms during incubation. Besides, stress factors disrupt pipping processes and hinder mass hatching of chicks to a great extent. All the aforesaid is determined in the first place by development of very dangerous oxidative stress reactions [1], which, inter alia, determine hormonal imbalance.

We chose «Klamin» preparation as a source of iodine. It contains this element in organic, easily accessible form. In the course of treatment of «Shaver 2000» crossing before incubation with a solution of this preparation, it has been established that the hatching of chicks definitely exceeds the control number by 9.19 % and hatchability of eggs - by 7.69 %, respectively. Moreover, the study of thyroid status showed that in the experimental group the level of thyroxin in the blood serum of day-old young was larger than the control number by a factor of 1.3 ($p<0.05$), and that of triiodothyronine– by 20 %.

Besides, in making an assessment of mass hatching of chicks it has been established that the process of hatching of species in the test group began 6 hours earlier and occurred more synchronously than in the control group. By the end of the 21st day of incubation (504 hours) almost all chicks (100 %) of the test group have hatched, and only 89.2 % of chicks of the control group have hatched by this time of incubation.

During the course of use of «Klamin» in the test group the increase of total antioxidant status index by 25 % was recorded, which determined the decrease of the level of secondary and final products of lipid peroxidation in the form of malondialdehyde-by 14.3 % and Schiff’s bases– by a factor of 1.7, compared to the control group.

Therefore, the use of iodinated «foodstuffs» for hen embryos is an effective way of increase and synchronization of hatching of chicks by means of prophylactics of excessive activation of free-radical processes.

1. Surai P.F., Fisinin V.I. Natural antioxidants in embryogenesis of hens and protection against stress in postnatal development // Agricultural Biol. 2013. No. 2. P. 3–18.

ELECTROCHEMICAL SYNTHESIS OF NEW DNA INTERCALATORS

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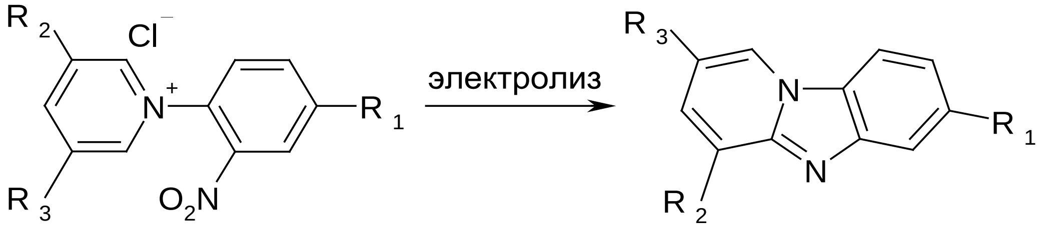
One important class of biologically active substances are DNA intercalators - compounds capable insert between adjacent pairs of bases in the DNA double helix. Such non-covalent interaction may lead to the suppression of the nucleic acid functions in physiological processes that find application in the chemotherapy of tumors.

DNA intercalators are planar polycyclic azaheterocycles, which is difficult to obtain. For the synthesis of such compounds in high yield and in pure form is required the use of highly reactive substrates and the absence of the side reactions. One promising approach to the synthesis of such structures is the formation of polycyclic fused system during reductive cyclization reaction. As substrates, we have proposed N-(2- nitrophenyl)pyridinium salts – easily available products obtained from the chemical industry. Containing in benzene ring nitro group reduces with cyclization and formation of C-N bond.

It is known that high reaction selectivity can be achieved by using electric current for substrate's conversion. Electrochemical method of the synthesis of biologically active substances also has such advantages as high thermodynamic efficiency and no waste disposal problems. Therefore, the electrolysis of N-(2- nitrophenyl)pyridinium chlorides (**1a-k**) was conducted to determine the possibility of obtaining condensed structures. The electrolyte was a mixture of 4% hydrochloric acid and an alcohol in a ratio of 1:1. Electrolysis was conducted in the galvanostatic mode, using a platinum anode, and a lead cathode. After passing 5-5.5 F*mole^{-1}, solution was made alkaline, and fused tricyclic products were isolated - substituted pyrido[1,2-α]benzimidazoles (**2a-k**). The identification of the structures were performed by NMR ^{1}H, ^{13}C and high resolution mass spectrometry (HRMS). The yields were 68-98 %.



1a-k **2a-k**

a R_1=CF_3, R_2=R_3=H, **b** R_1=CN, R_2=R_3=H, **c** R_1=$COOCH_3$, R_2=R_3=H, **d** R_1=$COOC_2H_5$, R_2=R_3=H, **e** R_1=COOPh, R_2=R_3=H, **i** R_1=CF_3, R_2=R_3=CH_3, **k** R_1=CN, R_2=R_3=CH_3

The resulting structures were investigated as potential DNA intercalators. 9-aminoacridine was used for comparative evaluation. This substance is known intercalator. Bioassay of compounds **2a-k** with the test object *L. grandiflorum* established that the substituted pyrido[1,2-α]benzimidazoles have a high affinity to nucleic acids (length of chromosomes have been increased in 2.7-3.6 times) in 1.5-2 times greater than 9-aminoacridine and therefore are effective DNA - intercalators.

The study was supported by the Ministry of Education and Science of the Russian Federation (project № 178 of research work YSU).

BIOACTIVE MATERIALS FOR MANUFACTURING OF MODERN IMPLANTS

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Orthopedic metal implants has long been successfully used in medical practice [1]. One of the effective ways to improve them is the applying of metal substrate by functional coatings. It is known that bioinert materials, such as stainless steel, titanium, etc., although being resistant to biochemical effects, *in vivo* can cause allergic reactions, and in the worst case rejection. To avoid these undesirable processes in cooperation with the experimental plant of Ilizarov Restorative Traumatology and Orthopaedics Centre the technological regulations for coating of NiTi on steel biospitsy for external fixation have been developed. The next step in improving the quality of the implants the use of biologically active materials similar in chemical composition to bone can be considered. The best of them is hydroxyapatite (HAP), which increases not only the strength of the implant, but also promotes bone formation [2]. In ISSC of RAS (UB) the composite material was created in which the role of the frame takes a highly porous titanium nikelid having good plastic and bioinert properties, and as a coating the HAP slurry was used. The synthesis of highly porous NiTi was performed by arc ion plasma deposition on NNV 6.6 I1 installation by interaction of precipitated titanium with porous nickel. The colloidal HAP was synthesized by precipitation from a solution of calcium hydroxide and phosphoric acid. The resulting dispersion was subjected to filtration, followed by aging of the isolated precipitate in air at room temperature. In the process of drying the dispersed system transform into HAP [3]. Since the precipitated HAP is partially decomposed at 800°C, we proposed methods of coating, excluding heat-treatment and allowing to maintain the phase composition and high biological activity of HAP. Of three methods only the vacuum impregnation with the following air-drying makes it possible to increase the mass of the sample to 45 wt. % in comparison with centrifugation and heat-treatment (43 wt. %) and sonication (33 wt. %). The coatings were examined by electron microscopy at scanning electron microscope JSM-6390 LA (JEOL, Japan).

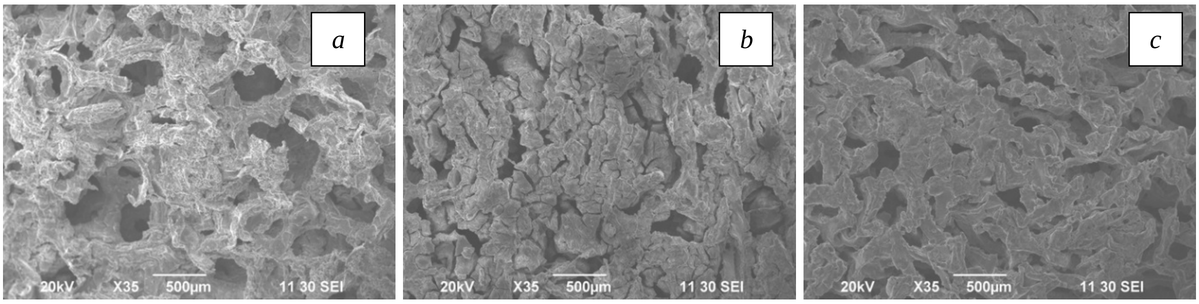

Fig. 1. SEM-images of biocomposite obtained by vacuum impregnation (a),
using centrifugation (b), sonication (c).

This work was partially supported by the scientific research program of the Ural Branch of RAS (projects 12-P-3-1003, 12-U-1008-3).

1. Kudinov V.V., Bobrov G.V. Coating deposition. Theory, technology and equipment. M.: Metallurgy, 1992. 187 p.
2. J. Black. Biomaterials. 1984. V. 5, No 1. P. 11–18.
3. Sabirzjanov N.A., Bogdanova E.A., Khonina T.G. RU patent No 2406693, 2010. Bull. No 35.

NEW CATIONIC CHLOROPHYLL *a* BASED NIR PHOTOSENSITIZER FOR ANTIMICROBIAL PHOTODYNAMIC INACTIVATION

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Photodynamic therapy (PDT) as well as antimicrobial photodynamic inactivation (PDI) is based on the administration of photosensitizing molecules which are preferentially accumulated in target tissues. Upon light activation, photosensitizers produce reactive singlet oxygen, which damages tumor or microbial cells. Subsequent oxidation-reduction reactions also produce superoxide anions and hydroxyl radicals responsible for tumor and microbial cell inactivation. The advantages of PDI are that resistance development in the target bacteria is improbable, and damage to adjacent host tissues and disruption of normal microflora can be avoided.

We have synthesized the cationic NIR photosensitizer (NIR-PS) on the base of *N*-aminopurpurinimide which we had prepared in our laboratory previously. The reaction conditions were optimized to prevent reduction of the vinyl group in pyrrole A. Introduction of nicotinic acid fragment and subsequent quaternization of the heterocycle nitrogen atom afforded the cationic photosensitizer.

Incubation of clinical isolate of multidrug-resistant *Pseudomonas aeruginosa* (*Bacillus pyocyaneus*, a leading nosocomial pathogen) with the potential NIR photosensitizer dissolved in Cremophor ELP with following visible light irradiation resulted in decrease in bacterial survival by two orders of magnitude. The efficiency of PDI using a cationic PS was also assessed on biofilms formed by uropathogenic *Pseudomonas aeruginosa*. The cationic sensitizer has shown to effectively photoinduce disintegration of the biofilm matrix and inactivation of microbial pathogens. It can be concluded that PDI using a cationic sensitizer has promising potential in the treatment of urinary tract infections.

We have synthesized the series of chlorophyll *a* based aminopurpurinimides containing polyamine moieties with different structures to be used as precursors for synthesis of polycationic PS with a potential application in treating pathogenic microorganisms.

APPROACHES TO TREATMENT AND PREVENTION OF CALCIUM OXALATE AND PHOSPHATES NEPHROLITHIASIS BY PHYTOPREPARATIONS

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Currently, clinical studies of urolithiasis increasingly developed, with particular attention to the etiologic and pathogenetic diagnosis of urolithiasis, as the basis for selecting the most effective treatment. The disease is one of the common pathologies and affects a large number of people in activism and age. A deep study of factors and finding effective treatment of urolithiasis is based on extensive use of the methodology is not only complex biomedical sciences including biochemistry, biophysics, immunology, genetics, but other possibilities and applied sciences sector – analytical and physical chemistry, bioorganic chemistry, phytochemistry, crystallography, computer science, modern instrumental methods of isolation and identification of complex native complexes and supramolecular assemblies of biologically active compounds. However, many questions concerning the causes and mechanisms of urolithiasis, are still unresolved. To some extent this is due to the polipatogenetic nature of urolithiasis clinically manifested in various forms and different features of the etiology and pathogenesis. Study of metabolic risk factors for disease underlie choice of tactics of conservative treatment to prevent stone recurrence. However, clinical experience shows that often urolithiasis develops in the absence of significant violations of urodynamics and metabolism. In this regard, much attention is given to studying the peculiarities of physical and chemical parameters of urine, largely determine the likelihood of crystal formation. Recent decades have seen changes in the treatment of nephrolithiasis issues. Widely used in clinical practice has received extracorporeal shock wave lithotripsy (ESWL), characterized by high efficiency and very low invasiveness, however, the use of this treatment method is complicated by the possibility of kidney damage, up to its rupture and perirenal hematoma formation. This causes the search relevance conservative, softer ways to influence nefrolity, in particular by means of methods of medical litholysis. Currently, for the treatment of urolithiasis has used drugs that are based on synthetic or natural bioactive substances or based on a combination thereof. However, the existing drugs do not have a high efficiency litholysis, especially regarding the dissolution of calcium oxalate stones. This causes the relevance of search, create and study new drugs litholytic ability is an important task of practical medicine, as it allows to exclude surgical intervention or reduce the number of ESWL sessions, which in turn will give the opportunity to avoid complications such as damage to the kidney tissues, of the phenomenon of "a stone walkway ", and nephrolithiasis recurrence of pyelonephritis.

FEATURES OF THE DESIGN OF EFFICIENT VETERINARY PROBIOTICS

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Global trend in most economically developed countries in the world is the growth of environment friendly products of livestock and poultry. The restrictions in the use of synthetic growth promoters, reducing the use of antibiotics and drugs of many other pharmacological groups are due to their potential adverse effects on the productive health status of animals. The development of effective and, at the same time, safe drugs and feed additives for animals, improving their physiological and biochemical status, is very promising direction. Such drugs include probiotic compositions that can improve the processes of digestion, metabolism, animal productivity increase the economic results of production, achieve environmental safety of products of animal origin.

In our country the works are carrying out in this direction. Russian veterinary probiotic “Laktobifadol ®” (Lactobifadolum ®) is the source of parietal intestinal microflora, contains 1 g of at least 80 million live cells of bifidobacteria (*B. adolescentis*) and 1 million live lactobacilli (*L. acidophilum*). The numerous studies were conducted by this probiotic construction, which have shown that microorganisms of these genera and species of healthy animals (including calves) prevail in the intestines and have the highest physiological relevance. Microorganisms belonging to the preparation “Laktobifadol ®”, forming organic acids, enzymes, vitamins, and other biologically active substances which favorably influence the physiological state of animals, improve feed conversion. Microorganisms belonging to the drug “Laktobifadol ®”, forming organic acids, enzymes, vitamins and other biologically active substances, which favorably influence the physiological state of animals, improve feed conversion. It is recommended to animals and birds at all ages, from the first days of life, promotes normalization of metabolism, the full realization of the genetic potential productivity. Used strains resistant in a wide range of pH and the presence of bile, phenol, high concentrations of NaCl. The bacteria don’t die in upper gastrointestinal tract and enter the intestines in active state, where they show biological activity. Special mode of sorption drying bacteria on bran or flour ensures their high ability to reproduction and move in the digestive tract, the rapid recovery of biological activity of bacteria. “Laktobifadol ®” acts also as a prebiotic, because it includes elements of the culture medium and the waste products of bacteria. They restore the intestinal mucosa, normalize digestion, stimulate metabolism. Production strains of microorganisms, including in “Laktobifadol ®”, are in a "protected" form, so the product can be used on the background of antibiotics, anthelmintics, coccidiostats. It can be used by “group method” in the mixture with fodder or milk replacer for production animal. The water-soluble form of “Laktobifadol ®” has been developed for the use in “watering” through medicator.

Thus, “Laktobifadol ®” normalizes the physiological composition and functions of ruminal microflora; does not contain synthetic additives and blends easily with premixes; suitable application by “group method” through technologically feed mixer, etc.

STUDY OF PHOTOPHYSICAL PROPERTIES OF METAL PHTHALOCYANINE NANO-AGGREGATES FOR THE APPLICATION IN THE EARLY DIAGNOSIS

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Traditionally, metal complexes of phthalocyanine (MPc) were developed for photodynamic therapy of cancer. Currently, interest has grown in the development of new diagnostic methods at early stages of various diseases, especially, for widespread atherosclerosis. To apply MPc in this area it is important to create biocompatible MPc systems and to study their photophysical properties. As the main carriers in such supramolecular systems were chosen polymers polyvinylpyrrolidone (PVP), polyethylene glycol (PEG), bovine serum albumin (BSA), and nano-sized silica (SiO_2).

Study of supramolecular systems showed that MPc can be in three states (monomer, H-, and J-aggregates) depending on the microenvironment, central metal ion and the presence of additional ligands. Because of the large ligand phthalocyanine zirconium all systems based on $Zr(OOC_{14}H_{27})_2Pc$ are entirely in monomeric state, as well as aluminum phthalocyanine AlClPc with the exception of SiO_2 system, where both $Zr(OOC_{14}H_{27})_2Pc$ and AlClPc have J-aggregates (λ=750 nm). Silicon phthalocyanine $SiCl_2Pc$ in PEG and SiO_2 forms J-aggregates (λ=850 nm). Magnesium phthalocyanine MgPc in PVP, PEG, SiO_2 presents monomeric state, and a small amount of J-aggregates (λ=830 nm). Vanadium phthalocyanine (V=OPc) in all supramolecular systems forms H-aggregates (λ=630 nm) and two types of J-aggregates (λ=730 and 830 nm).

Comparison of efficacy of different systems of AlClPc (Photosense ®, AlClPc-SiO_2 and AlClPc-PVP) showed that AlClPs-SiO_2 in 8.5 times more efficiently are accumulated with mesenchymal stromal cells in contrast to Photosense ® and 11 times for AlClPc-PVP. PcPVP in 0,3-3 µg/ml concentrations and Al-, MgPc-SiO_2 nanoparticles didn't affect cell viability while essential dark phototoxity of ZnPc-SiO_2 nanoparticles (in 100 ng/ml concentration and over) were demonstrated for human endothelial and mesenchymal stromal cells. Accumulation of MgPc-PVP was accompanied by reduction of mitochondrial potential in Lymph. Cell susceptibility to PDT with different Pc-nanoparticles varied. However, PDT with ZnPc-PVP and MgPc-SiO_2 was non-effective for all examined cell types while irradiation of AlPc-loaded cells with red light significantly decreased cell viability. Novel nano-particles with different properties were fabricated. ZnPc-PVP and MgPc-SiO_2 nano-particles may become a useful tool for diagnostics of different diseases while AlPc-SiO_2 nano-particles may significantly increase PDT efficacy.

This work was supported by the Russian Science Foundation (project No. 14-13-01351).

AN ALTERNATIVE SYNTHETIC APPROACH TO 2-AMINO-4-ARYLOXY-6-METHYLPYRIMIDINES AND THEIR WATER-SOLUBLE SALTS

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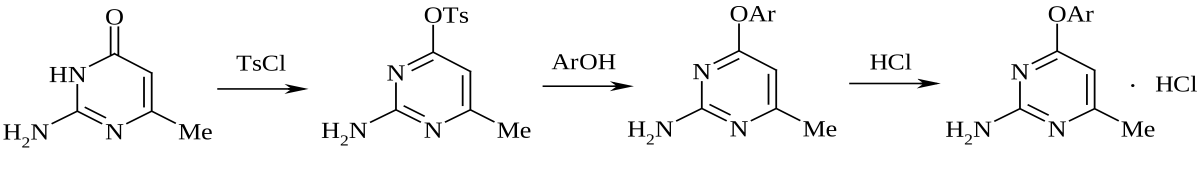
Many 2-amino-4-methylpyrimidine derivatives bearing a substituent in the 6-position of the ring have been obtained by nucleophilic displacement of the chlorine in 2-amino-4-chloro-6-methylpyrimidine (**1**). The same procedure was applied to the synthesis of some 2-amino-4-aryloxy-6-methylpyrimidines (**2**) [1]. In order to avoid exchange chlorination of 2-amino-6-methylpyrimidin-4(3*H*)-one (**3**) with highly toxic phosphorus oxychloride an alternative synthetic approach to the aryloxypyrimidines **2** was developed. This included a solvent-free condensation of 2-amino-4-tosyloxy-6-methylpyrimidine (**4**) with a variety of phenols at temperatures above 140^0C, followed by treating the reaction mixture with diluted alkali. No catalyst was required to force the reaction to proceed smoothly. In most cases the chromatographically pure aryloxypyrimidines **2** were isolated at least in 40% yield even when *ortho*-substituted phenols were used as reagents. All the products obtained were almost insoluble in water. ^{1}H-NMR spectroscopy was chosen as a method to confirm their structures.



3 **4** **2** **5**

Ar = $AlkC_6H_4$, $HlgC_6H_4$

The key intermediate **4** was readily produced by selective *O*-tosylation of the aminopyrimidinone **3** with tosyl chloride in an aqueous alkali solution at room temperature. Crystallization of the crude material from a benzene-cyclohexane mixture gave 30-35% yield of the pure compound **4**. A slightly better yield (*ca*. 45%) was achieved when crystallization was replaced with extraction in a Soxhlett apparatus. Since the yield of the tosyloxypyrimidine **4** was compared with that of the chloropyrimidine **1** [2], there appeared to be no need in using the latter as a starting material to generate the compounds **2**.

For increasing solubility of the aryloxypyrimidines **2** in aqueous media the salts thereof were prepared by dissolving the free bases in hydrochloric acid, followed by evaporation of the solvent if the corresponding hydrochlorides did not precipitate spontaneously. Among 2-amino-4-aryloxy-6-methylpyrimidinium chlorides (**5**) thus obtained, the compound **5** (Ar = $4\text{-}IC_6H_4$) was of the most interest as an oxygen analogue of 2-amino-4-(4-iodophenyl)amino-6-methylpyrimidine hydrochloride which was recently reported as a promising antitubercular agent [3].

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ELABORATION OF NEW APPROACHES TO THE SYNTHESIS OF BORON-PORPHYRIN CONJUGATES

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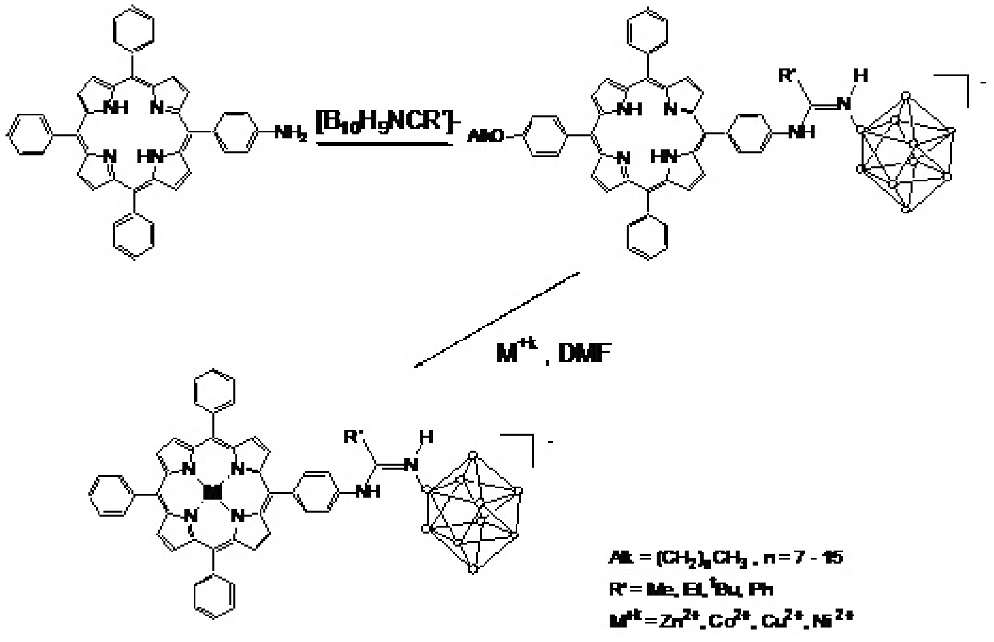
Porphyrins and relative compounds have been intensively studied because of their potential use in photodynamic therapy (PDT) and also using boron neutron capture therapy (BNCT). Amphiphilic porphyrin derivatives can selectively localize in tumor tissues because of their affinity to biological membranes. It is known that amino-group in porphyrins can be easily functionalized. This work is devoted to the synthesis of novel conjugates based on aminoporphyrins and closo-decaborate anions $[B10H10]^{2-}$ and investigation of their properties. In this work the series of aminoporphyrins possessing different number of $[B10H10]^{2-}$ anions were synthesized.



Scheme 1. Synthesis of mono-substituted boron-porphyrin conjugates.

Unsymmetrical aminoporphyrins containing one and two amino-groups were obtained by niration of tetraphenylporphyrin (TPP) by sodium nitrite and reduced using $SnCl_2$ into the corresponding aminoderivatives with high yields 70%. Tetranitroporphyrin were received by monopyrrole condensation of *p*-nitrobenzaldehyde and pyrrole in propionic acid with yields 30%, and then it was quantitatively reduced to the corresponding tetraaminoporphyrin. In the next step porphyrins were converted to the metal complexes with high yields (90–95%). Using the nucleophilic addition of aminosubstituted porphyrins to nitrile derivatives of *closo*-decaborate anion $[B_{10}H_{10}]^{2-}$ new assemblies containing boron and porphyrin fragments were obtained. In the resulting conjugates we varied the number of boron clusters and the nature of the metal-complexant. All compounds were identified by IR-, ^{1}H-, ^{11}B- and ^{13}C-NMR spectroscopy, ESI/MS, MALDI-TOF spectrometry.

This work supported by Russian Foundation for Basic Researches (project No. 13-03-00525a).

INTERACTION OF *D*-PSEUDOEPHEDRINE WITH 4-MORPHOLYL BENZALDEHYDE UNDER MICROWAVE ACTIVATION

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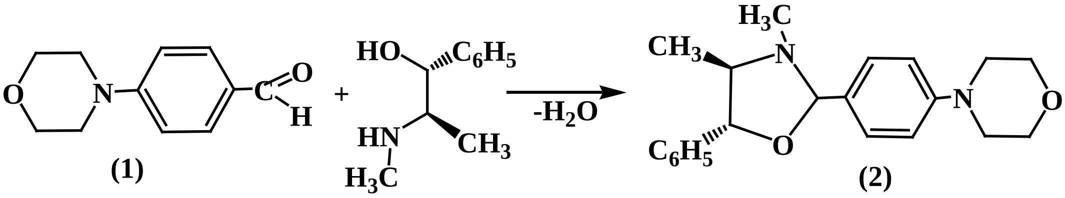
High interest to 1,3-oxazolidines is caused by the fact that these compounds posses unique properties which allow to use them for different practical purposes in medicine and industry, and they are of great scientific interest as the products of enantioselective synthesis of planar-chiral compounds. The absolute configurations of chiral centers of 1,3-oxazolidine compounds obtained on the basis of d- and l-ephedrines have been previously established by us [1]. We have studied the interaction of *D*-treo-2-methylamino-1-phenyl-1-propanol (the alkaloid of d-pseudoethedrine) **1** with 4-morpholylbenzaldehyde, which leads to the formation of oxazolidine **2** according to the following scheme:



As a result of the investigations of the influence of microwave field on reaction medium it has been established that during irradiation of the ethanol solution of reaction mixture for 15–20 min with pauses under at 500 Wt the process goes likewise stereoselectively (according to the results of TLC) with the formation of individual epimer (2) with the yield 95–98%. Physicochemical constants of oxazolidine (2) obtained by both methods (convectional heating and microwave activation) were identical. The results of TLC have shown that the only one product is formed as a result of the reaction.

Different configurations of chiral centers in the molecules of d- and l-ephedrines should lead to different conformations of oxazolidine cycle **2**. According to data of different researchers [2], the interaction of β-aminoalcohols with different aldehydes usually goes stereoselectively either with the formation of S-stereoisomer or R-epimer. The stereoselectivity of the process depends on the nature of reagents and solvents.

The structure of the compound **2** was studied on the basis of the results of IR- and ^{1}H NMR-spectroscopy (DMSO-d_6, 500 MHz). In the IR-spectra of the compound **2** there is no absorption band of hydroxyl and carbonyl groups of the initial reagents. On the basis of spectroscopic study of the structure of obtained oxazolidine **2**, it can be claimed that when interacting d-treo-2-methylamino-1-phenyl-1-propanol (alkaloid of d-pseudoethedrine) interacts with 4-morpholyl-benzaldehyde the oxazolidine **2** of S-configuration of C2 atom of oxazolidine cycle **1** is formed. It can most probably be the result of thermodynamic control of cyclization process, i.e. under conditions studied 2R-stereoisomers are sterically less favorable.

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SOLUBLE FORMS OF SOME DRUGS BASED ON SODIUM ALGINATE

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The necessity of imparting a medicinal product new properties caused widespread use of microencapsulation. Prolonged release from microcapsule, masking bitter and nauseating taste of substances, directed action of the drug, resistance to environmental factors - these and other properties of the substance reported by the microencapsulation methods.

This work is directed on giving to some substances of water-soluble properties, which as a consequence lead to increased bioavailability of the drug [1]. As the encapsulated substances was used a widely applied preparations in medicine such as furatsilin, levomitsitin, dibazol, tetracycline, metronidazole. These drugs belong to different classes of chemical compounds and possess various pharmacological effects. Among them are – broad-spectrum antibiotics, antibacterial, antispasmodic, antiprotozoal agents and immunomodulators. These agents are very sparingly soluble in water better solubility in ethanol and other organic solvents, sensitive to light.

As the shell for the microcapsules was selected a water-soluble polymer – Sodium alginate which, as expected, will allow water insoluble drugs translates into a shape forming a stable aqueous dispersion. This assumption was done because of the ability of alginate to gelation. Selection of alginate was determined being that its widespread use in medicine as auxiliary substances in the manufacture of finished dosage forms of drugs.

Microencapsulation was carried out physico-chemical method, which consists in reprecipitation of the polymer on the surface of the encapsulated substance by replacing the solvent.

To determine the conditions ensuring the best possible quality of formed product such parameters as the method of dispersing, the precipitant, pH of the reaction mixture et al. have been ranged. As a result of the analysis and processing of a large body of experimental data were selected optimum conditions of the microencapsulation process. Namely the use of mechanical (rather than ultrasonic) dispersing by a magnetic or overhead mixer and selection of ethyl alcohol as a precipitant, have allowed to increase the yield of the desired product, reduce the process time and reduce the size of the obtained capsules. Application of nonionic surfactants ensured the preservation of a stable dispersion, has prevented aggregation of individual capsules, whereby the product yield has increased.

The structure of isolated products was confirmed by infrared spectroscopy using FT-IR spectrometer type IR-200, equipped with a prefix of frustrated total internal reflection (FTIR). Quantitative analysis of the resulting microcapsules has been conducted by UV-spectroscopy on the spectrophotometer Shimadzu UV 1800 and also by HPLC with UV and mass detectors on a chromatograph Waters MSD SQD – ESI.

Thus, drugs encapsulated to a shell of sodium alginate significantly more resistant to environmental factors, and are capable to forming stable nanoparticulate suspensions visually indistinguishable from a true solution.

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SPECTRAL AND REDOX PROPERTIES OF DOUBLE-DECKER PHTHALOCYANINES FOR SENSOR DEVELOPMENT

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Double-decker phthalocyanine lanthanide complexes have a high stability, intense absorption and can be used in various technological and biomedical applications. Therefore, it is necessary to study the nature of the bands in the electronic absorption spectra, as well as the possibility of changing the spectral properties depending on the composition of multicomponent systems.

In this report, a correlation between the ionic radius of the metal in double-decker phthalocyanines and positions of Q-band maxima in the electronic absorption spectra was determined in dimethylformamide and chloroform. The increasing of ionic radius from holmium to lutetium resulted in a regular change in the position of the maxima of Q-bands in the absorption spectra.

In DMF Pc complexes exist in the negative (blue) form $[Pc^{2-}–M^{III}–Pc^{2-}]^{-}$. Complexes in solutions of $CHCl_3$ unlike solutions of DMF exist in the of neutral (green) form $[Pc^{2-}–M^{III}–Pc^{-}]^{0}$. This form is characterized by a band at λ ~470nm, which corresponds to the transition to e^{-} on π-orbital with the HOMO level.

In the case of lutetium and ytterbium diphthalocyanine partial oxidation in albumin solutions results in the appearance of the band at 660 nm. The intensity of this band increases proportional to the concentration of albumin. Such specific behavior of double-decker phthalocyanine complexes allows to consider them as promising materials for the development of sensor devices to determine albumin. Highly sensitive detection of albumin is of interest for the diagnosis of inflammatory processes, diabetes, and liver diseases.

Silica nanoparticles can be toxic to humans. The reduction process of the neutral form of phthalocyanine are observed in the presence of silica. This process can also be considered as a response to the silica nanoparticles. The observed spectral changes occur on the mechanisms of redox transitions between two forms (blue and green). The studied system can be regarded as a prototype sensor to albumin and silica nanoparticles to create sensors.

This work was supported by the Russian Science Foundation (project No. 14-13-01351).

SYNTHESIS OF CHLORINE *e*$_6$ AMIDE DERIVATIVES AND INVESTIGATION OF THEIR BIOLOGICAL ACTIVITY

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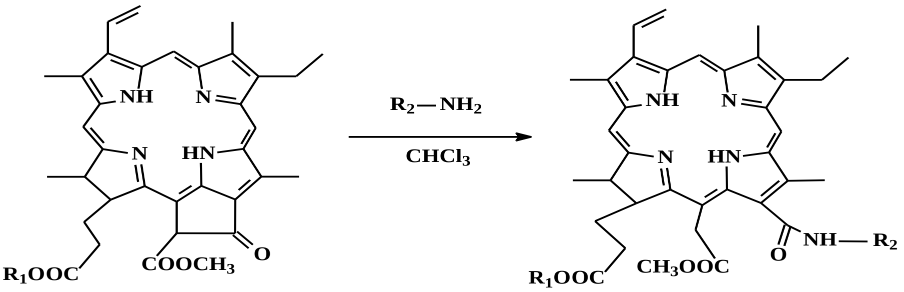
Photodynamic therapy (PDT) is a promising new treatment modality for several diseases, most notably cancer. In PDT, light, O_2, and a photosensitizing drug are combined to produce a selective therapeutic effect. Studies are underway to create new photosensitizer candidates, because the most commonly used porphyrin photosensitizers are far from ideal with respect to PDT. Finding a suitable photosensitizer is crucial in improving the efficiency of PDT. Chlorins seem to be promising candidates for photodynamic therapy (PDT) owing to their photophysical properties.

In this work, amide derivatives of chlorin *e*$_6$ are proposed as promising tetrapyrrole photosensitizers due to hydrophobic substituents which is believed determines the affinity of the photosensitizer to the cell membrane and contributes an embedding the molecules in the membrane systems and therefore the efficiency of photocatalytic processes increases. Given the above, the purpose of this study was to obtain derivatives of chlorin *e*$_6$ and to investigate their biological activity. To synthesize new photosensitizing drugs we carried out the disclosure of exocycle E of pheophorbide *a* and its methyl ester with primary unbranched aliphatic mono- and di- amines with the formation of the corresponding amide derivatives of chlorin *e*$_6$. The reactions yielded 45–60%.



1

2 a - o

R_2= a:$CH_2CH_2NH_2$, b:$CH_2CH_2N(CH_3)_2$, c:$(CH_2)_3N(CH_3)_2$, d:$(CH_2)_6NH_2$, e:$(CH_2)_2O(CH_2)_2O(CH_2)_2NH_2$, f:$(CH_2)_3CH_3$, g:$(CH_2)_4CH_3$, h:$(CH_2)_5CH_3$, i:$(CH_2)_6CH_3$, k:$(CH_2)_7CH_3$, m:$(CH_2)_8CH_3$, n:$(CH_2)_9CH_3$, o:$(CH_2)_{11}CH_3$

R_1 = CH_3 (a - e)
R_1 = H (f - o)

The purity and the structure of all the compounds obtained was confirmed by methods of TLC, electronic, IR, ^{1}H-NMR spectroscopy and mass-spectrometry.

The study of the biological activity of alkylamides of chlorin *e*$_6$ (**2f-2o**) was carried out on a biological model – the cells of two cultures: the ascitic form of mouse leukemia P-388 and human myelogenous leukemia K-562. As a result of the experiments all the PS studied showed low dark toxicity because the percentage of damaged cells was within the normal range (≈ 5-6%). In the investigation of phototoxic properties amides of chlorin *e*$_6$ containing 6 or 7 carbon atoms in the alkyl chain – 13(1)-N-hexylamid-15(2)-methyl ester of chlorin e$_6$ (**2h**) and 13(1)-N-heptylamid-15(2)-methyl ester of chlorin *e*$_6$ (**2i**) showed the highest photoactivity.

EVALUATION OF RESPIRABLE FRACTION DURING DEVELOPMENT OF FORMULATION FOR DRY POWDER INHALERS

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Development of a powder formulation for pulmonary drug delivery is currently an urgent problem due to the lack of reliable criteria to ensure successful intercommunication between the means of delivery (inhaler) and the delivered object – a powder composition comprising an inert carrier and micronized drug substance [1]. For each inhaler the powder formulation is different and is selected by experimental methods.

The results of Discus ® inhaler efficacy as compared with that of originally designed inhaler, obtained experimentally are presented here.

The original drug Seretide® and experimental formulation of salmeterol (d_{90} = 4,27 microns) and flutikozon (d_{90} = 5,00 microns) on the lactose carrier (Lactohale 230®: d_{10} = 5–15 microns d_{50} = 50–100 microns d_{90} = 120–160 microns) were used during the experiment. The components have been mixed for 5 minutes in Cyclomix 1L Hosokawa. Experimental mixtures were packed on the metering device Membrane TT, manufactured by Harro Hofliger

Respirable fraction output was measured at a constant air flow (60 l/min) using a Sympatec laser particle size analyzer, with and without the pre-separator installed. Selected research method allows to estimate the process of a dosage output: its duration and intensity: what makes it possible to compare the drugs by more criteria than using standard techniques (measurements using with Impaction devices).

Measurements without preseparator provide data on the dry aerosol composition at the initial stage of inhalation. Those with preseparator provide data on respirable fraction reaching the lung an integral over time from the product of the optical solid phase concentration and content of fraction of less than 5 microns was accepted for the quantitative estimation of the respirable fraction. Prepared in this way experimental data can be used for the qualitative comparison of different devices and inhaled dry powder formulation at a constant velocity of the inspiratory flow. The results of the experiments are shown below.

Test conditions	No preseparator		Preseparator installed	
	Seretide®	Cyclomix	Seretide®	Cyclomix
Discus ®	1965	1931	6410	4101
Inhaler of original design	3986	2924	8002	8745

Analysis of the obtained data allows to conclude that tha tan inhaler of original design allows to obtain an aerosol with a higher content of the respirable fraction.

The experimental formulation is preferable for the inhaler of original design. Discus ® inhaler shows the best results when working with Seretide ®.

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DEVELOPMENT OF TECHNOLOGY FOR THE FULLERENE C_{60}-CHLORIN

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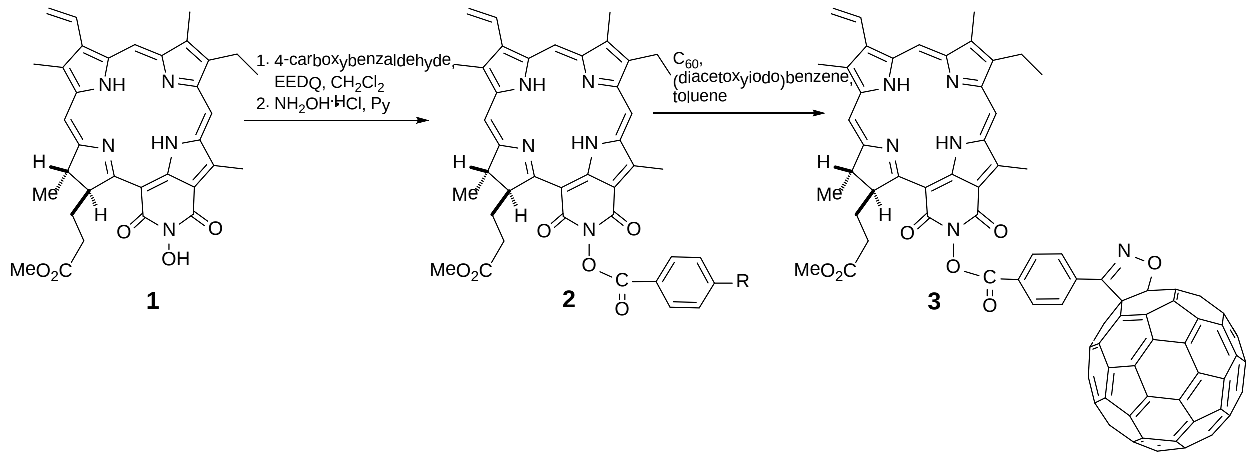
The unique mechanism of the nature occurring photosynthesis, implemented by the light-harvestig complex of the highly organized chlorophyll molecules multiplicity motivates to the creation of synthetic analogues able to transfer and convert the energy. In recent years scientists managed to synthesize molecule systems that successfully simulate some stages of naturally occurring solar energy conversion. Wherein the optimal components for creation such model systems are the chromophores, related to pigments taking part in the natural photosynthesis. The convenient photosynthesizing models are the covalent linked fullerene-chlorin dyads. The photoinduced electron transfer from the chlorin excited state (donor) to the fullerene (acceptor) occurring in such systems gives the state with the divided charges, modeling well the electron transfer during the photosynthesis process.

One of the most widely used methods of obtaining the fullerene-porphyrins and fullerene-chlorins is the 1,3-dipolar cycloaddition reaction. It is usually in the cycloaddition reaction to the double bonds of the fullerene enters the ylide generated by the condensation of N-methylglycine with formyl-substituted porphyrin or chlorin by prolonged refluxing in toluene. We used the convenient method of the 1,3-dipolar cycloaddition to the double bond of the fullerene nitrile oxide, prepared from hydroxyiminomethyl-substituted chlorin and (diacetoxyiodo)benzene, under mild conditions. As the initial substance for the conjugate synthesis the natural pigment chlorophyll *a* derivative, purpurin 18, was used. Chlorin p_6 13,15-*N*-hydroxycycloimide **1** was obtained by condensation of purpurin 18 methyl ester and hydroxylamine hydrochloride in pyridine. Compound **1** reacted with 4-carboxybenzaldehyde in the presence of 2-ethoxy-1-ethoxycarbonyl-1,2-dihydroquinoline (EEDQ) and the obtained formyl-containing chlorin was converted into corresponding hydroxyiminomethyl derivative **2**. Chlorin **2** reacted with (diacetoxyiodo)benzene and C_{60} in toluene at room temperature to form fullerene-chlorin **3** with 53% yield. The structure of the conjugate was characterized by ^{13}C NMR, mass-spectrometry and electronic absorption spectroscopy.



The results have been obtained within the framework of State task of the Ministry of Education and Science of the Russian Federation.

INNOVATIVE TECHNOLOGY OF MECHANOCHEMICAL PREPARATIONS FOR VETERINARY

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It is known that helminthiasis are particularly dangerous parasitic diseases, which in the world infected with more than 1 billion people (particularly in certain regions of the Russian Federation incidence ranges from 2 to 10% of the population). The main way of human infection with worms through contact with animals. According to WHO, the total number of illnesses and deaths from intestinal helminths higher than from bacterial, viral infections and other parasitic diseases combined [1].

To combat helminth animals commonly used as albendazole its various dosage forms [2]. The drug, possessing a wide range of actions, including against nematodes, cestodes and trematodes , used for the treatment of helminthiasis in different animal species. The disadvantage is the necessity of albendazole use it in relatively high doses and often increase the duration of the drug due to poor solubility in water and physiological media, i.e. effectiveness of albendazole drug reaches the theoretically possible. It should be noted that most of the substances used in practice or bad drugs are virtually insoluble in water and change the water solubility of these substances used physical (particle size reduction by grinding), chemical (pH change, the formation of the salt forms, complexation) and other methods [3].

We propose a method of solid-phase complexation, comprising by joint mechanochemical treatment albendazole substance with water soluble polymers in which there are obtained of supramolecular complexes albendazole: arabinogalactan = 1:5-20. These complexes are regarded as targeted delivery systems of anthelmintic drugs (s.c. Drug Delivery System).

The resulting system has increased the water solubilies of albendazole (up to 10^2 or more), which would require improvement and anthelmintic activity. And it was confirmed by the study of the nematocidic (*T. spiralis*), cestodic (*H. nana*) and trematodic (*F. hepatica)* activity complexes both in the laboratory and industrial experiments. The drug has a high activity (100%) while reducing the dose of albendazole in more than 10 times, in which the basic drug albendazole showed no anthelmintic action. Thus the toxicity of the complexes was 2-fold lower than that for the base albendazole.

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NEGATIVELY CHARGED NUCLEIC ACID MIMICS BASED ON GLUTAMIC ACID: SYNTHESIS AND PROPERTIES

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A great number of methods in molecular biology and diagnostics are based on binding of a molecular beacon with a "target" complementary nucleic acid fragment. Peptide nucleic acids (PNA, Figure 1b) play an important role in DNA hybridization-based technologies. It has been shown previously that the properties of chiral PNA (Figure 1c,d) depend on the configuration (R or S) of a chiral center and its position in the pseudopeptide fragment (α- or γ -). What is more, single-stranded PNA oligomers may be preorganized, i.e. adopt the helical structure, if they contain chiral centers. At the same time, functional groups of the side residues impart additional properties to chiral PNA.

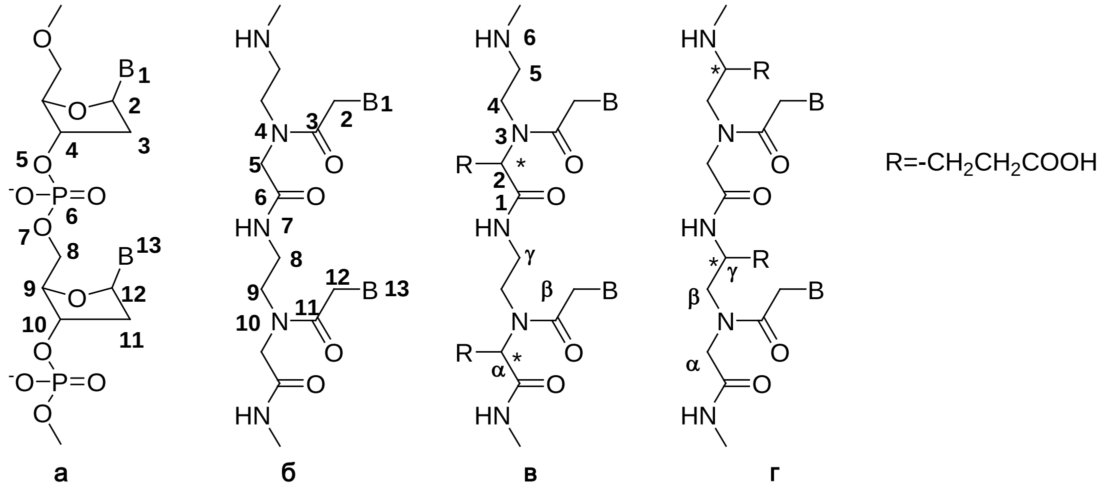

Figure 1. Fragments of DNA (а), «classical» PNA (б), chiral α-PNA (в) and chiral γ-PNA (г).
B= Ade, Gua, Thy, Cyt.

In our studies, we developed methods for obtaining a new structural modification of nucleic acids – negatively charged peptide nucleic acids (Figure 1в,г). Regular distribution of the negative charge, introduced via the carboxyethyl side group, and the maintenance of the internucleobase distance characteristic of native nucleic acids makes the new modification of "classical" PNA a relatively close mimic of native oligonucleotides. Introduction of negative charges into PNA backbone not only allows us to solve the problems of solubility and self-aggregation at particular pH values, but also ensures increased specificity of PNA binding to nucleic acids and enables us to control the hybridization process by changing ionic strength of a solution.

The synthetic part of our work was aimed at consecutive development of methodology for obtaining all structural components of PNA – pseudopeptides, monomers and some oligomers of α- and γ-series. Model studies included optimization of the Boc-protocol of solid-phase oligomer synthesis. Chromatographic and physicochemical analytical methods were used to control chemical conversions and to confirm the structures of the newly synthesized compounds. Hybridization properties of the new negatively charged PNA oligomers were investigated. The results of our work suggest that γ-derivatives are generally more promising for constructing DNA mimics with a predetermined structure than α-isomers.

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STUDY OF INTERACTION BETWEEN CHLOROPHYLL AND PHOTOSENSITIVE ELECTRON ACCEPTORS

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Interaction between natural and synthetic porphyrins and biologically active compounds involving the transfer of electrons and energy plays a very important role in photobiological and photomedical processes. During photosynthesis in nature, the electrons from a chlorophyll molecule in singlet-excited state are transferred in sequence along the electron transport chain with the help of such reverse electron transporters as nicotinamide adenine dinucleotide phosphate and quinine derivatives.

This work presents the study of interaction between a chlorophyll and photosensitive electron acceptors nicotinamide adenine dinucleotide phosphate (NADP) and 2-methyl-1,4-naphthoquinone (vitamin K_3, MNQ) over a wide range of concentrations, carried out with the help of spectral methods. Chlorophyll – 2-methyl-1,4-naphtho-quinone ethanol solutions (C_{Chl} = 1Ч10^{-5} M and C_{MNQ} = 6.7Ч10^{-5} ч 1Ч10^{-1} M) and chlorophyll - nicotinamide adenine dinucleotide phosphate aqueous-ethanol solutions (C_{Chl} = 1Ч10^{-5} M and C_{NADP} = 5Ч10^{-6} ч 5Ч10^{-3} M) were used in our experiments. Absorption spectra (200-900 nm) were recorded on a TU-1901 UV-Vis spectrophotometer from Beijing Purkinje General Instruments Co Ltd. Poorly resolved spectra were analyzed by decomposing the spectra into their Gaussian constituents. The fluorescence spectra in the range of 600–800 nm were recorded on a Fluorat-02-Panorama set-up (Lumex). The excitation wavelength was 430 nm. All measurements were conducted at room temperature in standard K10 quartz cuvettes with optical path lengths of 1 cm.

From the character of the changes in the chlorophyll absorption and fluorescence spectra caused by adding nicotinamide adenine dinucleotide phosphate and 2-methyl-1,4-naphtho-quinone one can see that coordination interaction occurs with the participation of the conjugated system of double bonds of the chlorophyll heteromacrocycle, since the frontier orbitals of the chlorophyll are localized on the ligand and do not include magnesium ions [1]. Photoinduced charge separation occurs in aqueous ethanol solutions of chlorophyll and nicotinamide adenine dinucleotide phosphate, resulting in dynamic quenching of chlorophyll fluorescence. Coordination interaction between chlorophyll and nicotinamide adenine dinucleotide phosphate is established at a nicotinamide adenine dinucleotide phosphate concentration of $C_{\mathrm{NADP}} \geq$ 5Ч10^{-4} M. The nonlinear Stern-Volmer dependence in this range is due to input from static quenching. The quenching of chlorophyll fluorescence in an 2-methyl-1,4-naphtho-quinone (C_{MNQ} = 6.7Ч10^{-5} ч 1Ч10^{-4} M) solution is described by a linear dependence in the Stern-Volmer coordinates. No complex formations are observed for this system and electron transfer is of the dynamic type. At elevated 2-methyl-1,4-naphtho-quinone concentrations static or mixed-type energy transfer from 2-methyl-1,4-naphtho-quinone to chlorophyll is observed.

These data testify that the photophysical properties of biologically and pharmaceutically active tetrapyrroles depend largely on the nature and relative quantity of the photo- and redox-active compounds present in multicomponent biological systems.

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PREPARATION OF THE SUBMICRON PECTINATE PARTICLES WITH MIRAMISTIN

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At present time there is a great interest to polymeric carriers for drugs. Entrapment of miramistin (*Mir*), possessing antimicrobic activity, in hydrogels considerably enhances its medical efficiency [1]. Natural biodegradable and biocompatible polysaccharides are one of the perspective materials for creation of drug carriers. We have previously shown that gel particles based on amidated pectin can entrap up to 50 wt. % antitumor drug imatinib methanesulfonate [2].

The aim of this work is the creation of calcium pectinate gel particles, containing antiseptic drug miramistin. Submicron particles were synthesized by ionotropic gelation by crosslinking the pectin macromolecules (degree of esterification 35-42%) with calcium cations [3]. Miramistin was included into the obtained gel particles from its aqueous solutions with various concentrations (table). The *Mir* entrapment efficiency (EE) was calculated by the equation: $EE = (m_0-m_1)/m_0 \cdot 100$, where m_0 and m_1 is the quantity of miramistin in the initial solution and in the supernatant after entrapment, respectively, mg.

Depending on the amount of miramistin in solution its entrapment efficiency into the particles is 68-92% (table). Increase in miramistin concentration in aqueous solution from 0.3 to 3.3 mg/ml leads to rising in its amount in the particles in 7 times and reaches up to 70 wt.%. Entrapment of miramistin in the calcium pectinate particles results in the reduction of the absolute values of ζ-potential: from – (18,0 ± 3,0) mV for initial particles to – (13,5 ± 0,5) mV for the particles, containing 70 wt.% of miramistin.

The amount of miramistin in the calcium pectinate particles

Concentration of aqueous solution of miramistin, mg/ml	Entrapment efficiency of miramistin, %	Amount of miramistin in the particles, wt.%
0,3	68,0±1,4	9,8±0,4
0,4	82,5±0,7	18,0±1,4
0,5	82,5±6,4	21,0±1,4
0,8	82,0±4,2	28,0±7,1
1,0	80,0±5,7	31,0±4,2
1,6	91,5±2,1	51,0±0,1
3,3	86,5±0,7	70,5±4,9

Thus, submicron calcium pectinate particles (60–120 nm) with defined amount of miramistin (from 10 to 70 wt.%) were obtained in the form of colloids and lyophilized powders.

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NEW APPROACH TO THE SYNTHESIS OF BIOLOGICALLY ACTIVE DERIVATIVES OF PHOSPHORYLACETIC ACIDS

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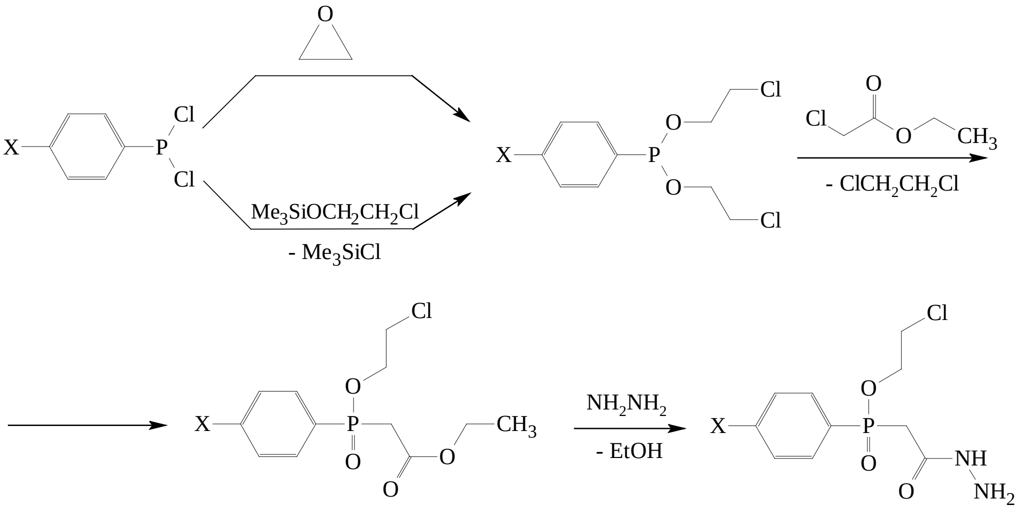
Biological activity of phosphorylacetic acids was detected in the 60s of the last century [1]. Of special interest are phosphorylacetic acid hydrazides – Phosenazid (2-diphenylphosphoryl)acetic acid hydrazide) and CAPAH (2-[4-(dimethylamino)phenyl](2-chloroethoxy)phosphorylacetic acid hydrazide). Phosenazid was recommended for wide clinical use as a tranquilizer and antialcoholic agent. In the stage of experimental investigation, CAPAH showed neuroprotector and antidepressant activities.

Method of preparation of these compounds is based on reaction of corresponding arylchlorophosphines with ethylene oxide, treatment halogenacetic ester and then hydrazine hydrate [2]. Drawback of this method are specific properties of oxirane – it is extremely flammable and its mixture with air are explosive.

To avoid that we investigated the possibility of replacing the oxirane on trimethylsilyl ethers of alcohols with different structure [3]. In this work we investigated this method on the example of synthesis of CAPAH and its analogies.



X = H, Cl, $N(CH_3)_2$

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4-(3H-1,2-DITHIOLE-3-THIONE-5-YL)PHENYL ESTERS OF ACRIDONE CARBOXYLIC ACIDS

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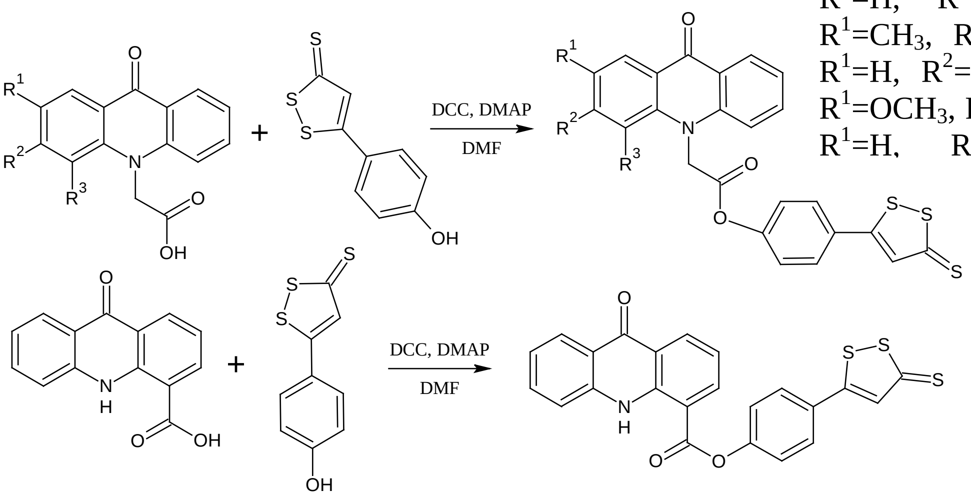
Acridone derivatives – an important class of heterocyclic organic compounds and many of them have some useful pharmacological properties. For example, acridoneacetic acid (AAA) derivatives and 4-carboxyacridone (4-CA) exhibit antiviral, antibacterial and antitumor activity [1, 2]. The derivatives of 5-(4-hydroxyphenyl)-3H-1,2-dithiole-3-thione (ADT-OH), which is widely used as H_2S-releasing compound in the organisms for the synthesis of pharmaceutical hybrids, were actively studied last years. It was found that 4-(3H-1,2-dithiole-3-thione-5-yl)phenyl esters of various carboxylic acids show anti-inflammatory and antitumour activity. Therefore, the search for new potential biologically active substances in these series of compounds is very promising scientific task.

We synthesized 4-(3H-1,2-dithiole-3-thione-5-yl)phenyl esters of AAA and 4-CA according to the following scheme:

R^1=H, R^2=H, R^3=H;
R^1=CH_3, R^2=H, R^3=H;
R^1=H, R^2=H, R^3=CH_3;
R^1=OCH_3, R^2=H, R^3=H;
R^1=H, R^2= OCH_3,



The desired products were obtained in DMF in the presence of N,N-dicyclohexylcarbodiimide (DCC) and a catalytic amount of N,N-dimethylaminopyridine (DMAP) at room temperature for 10 hours. The precipitate of N,N-dicyclohexylurea was filtered, the filtrate was poured into water. The resulting precipitate was filtered off and washed with a hot solution of $CHCl_3$. This synthetic method seems most convenient because it does not require a complicated purification of the final products and provides high yields.

Investigation of the antibacterial activity of acridoneacetic acid's 4-(3H-1,2-dithiol-3-thione-5-yl)phenyl ester against the test strains of pathogenic microorganisms has indicated that this compound has moderate antimicrobial activity.

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NEW BIOLOGICALLY ACTIVE DERIVATIVES OF 10H-9-ACRIDANONES

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The series of biologically active compounds containing a structural fragment 10H-9-acridanones were synthesized.

The methods of synthesis of diphenylamine-2-carboxylic acids as initial substances for the synthesis of acridanones were improved. It is shown that the use of the microwave and ultrasonic activation leads to the increasing of the yield of product and reduction of time of reaction [1].

The kinetic parameters of cyclization of 2r- and 4r-substituted diphenylamine-2-carboxylic acids in sulfuric and polyphosphoric acid were determined. It is shown that the rate of cyclization of diphenylamine-2-carboxylic acids is linearly dependent on the nature of substituents in the meta-position relative to the reaction site in accordance with the two parameter Hammett equation.

The cyclization of diphenylamine-2-carboxylic acid under microwave and ultrasonic radiation was investigated. The features of acridanones synthesis under thermal conditions and under microwave and ultrasonic activation were compared. The kinetic parameters of the processes were measured. Was found that the use of microwave and ultrasonic radiation allowed to shorten time of reaction and to increase the yield of reaction’s product. The optimal conditions for processes were determined.

Sulfonic acids of substituted acridanones were got. Sulfonation of 10-carboxymethylene-9-acridanone under thermal and microwave conditions was studied. The rate constants of the accumulation of the desired product in the reaction conditions were measured. By a method NMR ^{1}H their structure is set. It is shown that acridanonsulfonic acids possess moderate antibacterial activity and able to stimulate the the germination of cereals.

The rows of derivatives of substituted acridanonecarboxylic acids - amides, ethers, arylidenhydrazides, oxadiazoles and other were got. Antibacterial activity of the got substances is investigational. For some substances antibacterial activity is exceeding activity of standard drug of acridine row of rivanol [2].

It is shown that N- acridinylated derivatives of meglumine (*1*-deoxy-l-methylamino-D-glucitol), and also his amides - the derivatives of - of N 9-acridinylglycine possess very considerable antimicrobial activity, exceeding corresponding indexes for well-known and widely used drug of acridine row - of 2-etoxy- 6, 9-diaminoacridine lactat (rivanol) and comparable with (±)-ofloxacin.

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THE HYDROGENATION OF MONO- AND DISACCHARIDES USING NANOSTRUCTURED POLYMER-BASED Ru-CONTAINING CATALYST

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The catalytic hydrogenation of mono- and disaccharides, such as D-xylose, D-lactose and D-maltose, is an important technological process to produce sugar alcohols which are used in the food and pharmaceutical industries.

The main catalyst used for the hydrogenation of mono- and disaccharides is Ni-Raney, but despite of the low cost it has a lot of disadvantages, for example leaching of active phase and surface decontamination due to the formation of the polymeric film [1]. Respectively, technologies based on Ni-Reney using include difficult purification steps of product and regeneration of the catalyst. One of the possible ways to solution of this problem might be applying of highly dispersed ruthenium catalysts on the different supports [2]. The use of hypercrosslinked polymers such as hypercrosslinked polystyrene (HPS) as a support is the most promising way.

Therefore it's important to investigate the ruthenium-containing nanoparticles formed in pores of HPS in the mono- and disaccharides hydrogenation process.

The hydrogenation of D-xylose, D-lactose and D-maltose was carried out in a wide range of conditions varying temperature from 100 to 150˚C, the hydrogen pressure from 10 to 120 bar, substrate concentration from 0.1 to 0.5 mol/l, the metal loading in the catalyst 1.1 – 4.9 wt.%.

Optimal results were obtained:

- for D-xylose hydrogenation (conversion – 99.9 % and selectivity – 98%): the catalyst – MN-100/Ru-2.85% (wt.), T = 140˚C, P_{H2} = 40 bar, $C_{D\text{-xylose}}$ = 0.4 mol/l, C_{cat} = 1.3 g/l;

- for D-lactose hydrogenation (conversion – 98 % and selectivity – 97%): the catalyst – MN-100/Ru-2.85% (wt.), T = 100˚C, P_{H2} = 50 bar, $C_{D\text{-lactose}}$ = 0.5 mol/l, C_{cat} = 1.3 g/l.

- for D-maltose hydrogenation (conversion – 99 % and selectivity – 96%): the catalyst – MN-100/Ru-2.85% (wt.), T = 140˚C, P_{H2} = 40 bar, $C_{D\text{-maltose}}$ = 0.4 mol/l, C_{cat} = 8 g/l.

As a result of investigation, it was found that the synthesized catalytic systems based on Ru-containing nanoparticles stabilized in HPS matrix are promising for selective hydrogenation of mono- and disaccharides. The use of HPS functionalized with amino-groups as catalytic support provides high activity and selectivity of the catalysts.

Acknowledgements:

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THE STUDYING OF STRUCTURE AND CHARACTERISTICS OF COMPLEX COMPOUNDS OF Cu^{2+} AND Fe^{2+} WITH METRONIDAZOLE DERIVATIVES

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Metronidazole is one of clinically significant antibacterial drug of a number of the nitroimidazole, finding application in medicine as anti-inflammatory and antifungal remedy. The chemical structure of metronidazole causes its ligandny properties in complex formation reactions due to donor atom of nitrogen in a five-membered cycle [1,3]. For coordination compounds of metal ions with metronidazole derivatives: (2-(5-nitro-1H-imidazole-1-yl) ethyl 2-(9-tioksoakridin-10 (9H) - yl) acetate (L_1), 2-metoxy-N-(2-(2-methyl-5-nitro-1H-imidazole-1-yl)ethyl) acridin-9-amine (L_2), 2-(2-methyl-5-nitro-1H-imidazole-1-yl) ethyl-2-((3-(2-(2-methyl-5-nitro-1H-imidazole-1-yl) carbonyl) phenyl) amine) benzoate (L_3), 2-(2-methyl-5-nitro-1H-imidazole-1-yl) ethyl 2-((3-((2-(2-methyl-5-nitro-1H-imidazole-1-yl) ethoxy) carbonyl) phenyl) amine) benzoate (L_4), possessing antibacterial activity [2], probably mutual strengthening of these properties.

Spectrophotometric method defined conditional constants of a deprotonization of derivatives of metronidazole at various ionic force; extrapolation of the received values on the zero ionic force of solutions calculated values of constants of a deprotonization.

Complex connections of derivatives of metronidazole with cations of iron and copper were received in water- ethanol solution in the range pH 3 – 7,5. Studying of reactions of a complexation carried out the UV-spectroscopy method. Structure of complexes was determined by a saturation curve at constant concentration of a ligand: for copper and iron cations Me : L = 1:1 relation. According to Komary's method conditional constants of stability of the received complex connections of metronidazole derivatives with copper cations were calculated: (P=0,95, n=5): β' (ML_1) $=2{,}95*10^5\pm0{,}07*10^5$; β' (ML_2) $=4{,}39*10^6\pm$ $0{,}81*10^6$; β' (ML_3) $= 2{,}76*10^5\pm0{,}16*10^5$; β' (ML_4) $= 2{,}77*10^5\pm0{,}36*10^5$ and with iron cations: β' (ML_1) $= 1{,}57*10^5\pm0{,}34*10^5$; β' $(ML_2) = 0{,}29*10^5\pm2{,}49*10^3$; β' $(ML_3) = 1{,}82*10^5\pm1{,}4*10^4$; β' $(ML_4) = 0{,}25*10^5\pm0{,}05*10^5$.

In comparison with ranges of reagents in IR- spectrums of complexes the emergence of additional strips in the field of 1200–1300 cm^{-1} is observed. It gives the chance to assume that in molecules of ligands as a site of binding nitrogen of a five-membered cycle of a metronidazole fragment of connections acts.

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STUDY SUBLIMATION OF BINARY MIXTURES RUBBER ACCELERATORS

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Organic accelerators of sulfur vulcanization of rubbers – are molecular crystals. When mixed and heated these accelerators, can be prepared a eutectic mixture or solid solution substitutions. Binary eutectics have the property of granulation. This indicator is important for greening technologies on preparatory production.

In this regard, we have conducted researchs for binary systems accelerators. As such as: tetramethylthiuram disulfide (TMTD) – 2 benztiazolilsulfenamid (CBS), benzothiazole, 2,2-dithiobis- (DBTD) – TMTD, 2-mercaptobenzothiazole (MBT) – TMTD.

The results showed that granulation of these systems accelerators in rubber compounds may be in proportions corresponding to the interval between two eutectic melting temperatures. At a temperature of 111°C [1], on the phase diagram of a binary mixture have characterized by the formation of eutectic. This indicates the formation of a eutectic melt of new chemical compounds.

Based on studies sublimation vulcanization accelerators rubber compounds, we can propose the following ways to reduce their emissions during storage and transport [2]:

- preparation the mechanical of mixtures of accelerators and zinc oxide in the desired ratios;
- preparation fusible and solid granules obtained from eutectic melts of binary mixtures of ingredients. At that this sublimation occurs only from the surface of the granules;
- transportation and storage of the last in a sealed container in view of the saturated vapor pressure accelerators.

As a result, the above method can substantially reduce adverse effects. These adverse events may lead to contamination of the environment due to the emission of highly toxic sulfur vulcanization accelerators rubbers.

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PREVENTIVE AND MEDICATIVE EFFECTS OF ANTIOXIDANT BIENZYME CONJUGATE USED AT ENDOTOXIC SHOCK IN RATS

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Cardiovascular injuries have been going along with oxidative stress as usually. The intense research of antioxidants is performed for blocking oxidative stress. Advances of antioxidant studies contribute the formation of antioxidant therapy. The antioxidant enzymes (as superoxide dismutase /SOD/ and catalase /CAT/) are significant potential agents for this therapeutic aim.

We obtained the bienzyme conjugate using the attachment of SOD to CAT via chondroitin sulphate (CHS). The SOD-CHS-CAT conjugate had prophylaxis and preventive actions after intravenous administration of hydrogen peroxide in rabbits and rats. It should be noted the oxidative stress accompanies for development of endotoxic shock. In this case the inflammatory reactions of organism are going along with pronounced oxidative stress. There is the model of septic shock of animals due to administration of bacterial lipopolysaccharide (LPS) them as provoking infectious agent.

The therapeutic effect of bienzyme SOD-CHS-CAT conjugate has special research interest associated with activity of conjugate after preventive and medicative administration (i.e. before and after LPS administration). This approach allows experimentally to determine the area of potential destinations of assayed derivative that was the aim of our research.

The SOD-CHS-CAT conjugate demonstrated the influence on cytokine (but not previous neurological) phase of LPS injury and its belated stages after intravenous administration at preventive regime. It is expedient to evaluate in vivo the SOD-CHS-CAT effect after its medicative administration (i.e. after, but not before LPS administration). The effect of bienzyme conjugate administered in medicative regime had increased the survival of rats for endotoxic shock. It was the expressive efficacy of medicinal employment of SOD-CHS-CAT conjugate.

Therapeutic using antioxidant means is effective not only for preventive but also for medicative regime and important for consequent investigation.

This research was supported in part by RFBR (grant 12-08-00010) and by the Ministry of Health Care of the Russian Federation.

THE STUDY OF APPLICATION OF PEROXIDASE IMMOBILIZED ON MAGNETIC NANOPARTICLES

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Currently, the significant gains in the immobilization of enzymes were achieved. It allows to reuse the expensive enzymes. But traditional methods of separation of heterogeneous systems (filtration and centrifugation) contribute the significant deactivation of immobilized enzyme [1, 2].

Magnetic nanoparticles are the promising alternative to traditional supports for the enzymes immobilization. Magnetic separation of immobilized enzymes not only increases the enzymes stability, but also reduces the number of chemical-technological processes of separation stages (filtration or centrifugation) [3].

In this paper an effective way of peroxidase (EC 1.11.07) (HRP) immobilization on magnetic nanoparticles Fe_3O_4 is investigated in the oxidation reaction of 2,3,6-trimethylphenol (TMF) to 2,3,5-trimethylhydroquinone (TMHQ) (precursor of vitamin E). Immobilization of HRP was performed on nanoparticles by precipitation of previously synthesized Fe^{2+} and Fe^{3+} in an alkaline medium , stabilized by sodium citrate and activated by 3-aminopropyltriethoxysilane. The advantages of such biocatalyst using include easy separation of oxidation products from the reaction medium by external magnetic fields.

The effect of pH and temperature on the rate of TMHQ production was also studied in this investigation. Biocatalyst exhibits the highest activity at pH 6.5. The optimum temperature is $40^{o}C$. The biocatalyst activity decreases only to 29% during the 10 cycles.

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SEPARATION TECHNOLOGY OF ESSENTIAL OILS FROM PLANTS *“PIMPINELLA ANISUM* L.” CULTIVATED IN UZBEKISTAN

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Essential oils are valuable natural products obtained from aromatic plants in connection with their use in perfumery, food industry and medicine for the treatment of various diseases.

In connection with this the separation of essential oils from aromatic plants cultivated in Uzbekistan is an actual problem.

The aim of the present work is to optimize the separation of essential oils from plants, “*Pimpinella anisum* L.” cultivated in Uzbekistan.

The separation technology of essential oils is based on the sublimation of volatile components. To do this, dried and ground aboveground part of plant “*Pimpinella anisum* L.” has been used. The sample of 1 kg was placed in a round bottom flask of 5 liter. The flask was heated with a sand bath upto 200°C with continoues mixing of the sample. During heating volatiling volatile components passes through the condenser and collected in the receiver. After appropriate purification and drying (by sodium sulfate) the oils have the following physical-chemical properties: density – 0,983±0,005 g/ml; refractive index – 1,556±0,004; optical rotation at 20°C – from +2 to -1 degrees.

The composition of essential oil was determined by gas chromato-mass-spectrometry.

To optimize the separation process of essential oils the grounding level of the plants, the process temperature and stirring rate, as well as the process time have been used. On the basis of the compiled model the best conditions for the separation of essential oil from aboveground part of the plant “*Pimpinella anisum* L.”: d = 1h2 mm; t = 160-165°C; v_{mixing}= 48 h 60 rev/min; τ = 12 h 15 min. The separated oil has been transferred for the use in medicine, for the purposes of aromatherapy.

This work was supported by grant ITD-12-64.

THE NEW PRINCIPLE OF "GREEN CHEMISTRY". THE DEVELOPMENT OF NEW SYNTHESIS IDEOLOGY OF HIGHLY FUNCTIONAL CHARGED SYNTHONS

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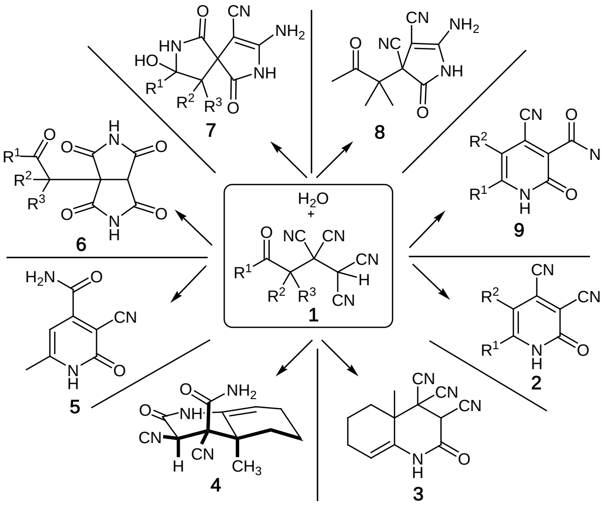
The turnover of organic compounds in various industries is enormous. They include hundreds of thousands of drugs, antibiotics, pesticides, monomers. It is trillions of dollars in terms of value. All newer generations are more complex than previous ones and impose additional chemical and technological processes of their production. In accordance with the concept of "green chemistry", it should include fewer stages of drug production and it should present waste-free technology. The use of catalysts is regarded as the method of its realization. However not all processes are catalytic that is why we propose to introduce and put into practice the use of new functionally charged (FCh) and functional- structural charged synthons (FSChS) . From our point of view a cyano group (carbonitrile) possesses the highest and easily accessible energy for chemical reactions multiple bonds of which can be employed in a variety of chemical transformations. Triple bond in carbonitrile accumulates the energy of 212 kcal/mol (more than triple carbon-carbon bond). The cyano group is compact – 3.5 Å, it does not create steric hindrance in the reactions and extremely acceptor. It is cyano and oxo groups that once created the necessary set of vital amino and nucleic acids, monosaccharides in the prebiotic period of organic life in hydrocyanic acid and formaldehyde. All other characteristic groups and organic chemistry in general were created on the basis of their interactions and recombinations. They are *paterfamilias* of almost all classes of organic compounds. Occasionally some groups of researchers dealt with this amazing group but no one consciously proclaimed the principle of energy usage and its links for "greening" our "brown” organic chemistry. We develop the concept of purposeful creation of new and existing FChS and FSChS containing several cyano- and oxo- groups as well as their investigation. We obtained hexacyanocyclopropane the potential energy of which is 6×212+27(cycle) =1299 kcal/mol. The potential energy can easily be used (our works) in a variety of intramolecular processes with speeds often correlating to enzymatic ones. It is clear from all above mentioned that a single process step can implement numerous chemical intramolecular like "dominoes", "push- pooled processes". We have shown the possibilities of intramolecular interactions from 1 to all 4-cyano groups on the example of FChS, the reactions 4-(1,1,2,2)-oxoalkan tetracarbonitrile-1 with water. The reactions occur quickly often with quantitative yields.



USING 8-OXO-2'-DEOXYGUANOSINE AS A BIOMARKER OF OXIDATIVE STRESS IN THE PATOLOGY AND CHECK OF MEDICINES' EFFECTS

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There is extensive experimental evidence that oxidative damage constantly occurs to lipids of cellular membranes, proteins, and DNA. In nuclear and mitochondrial DNA, 8-hydroxy-2'-deoxyguanosine (8-OH-dG) or 8-oxo-7,8-dihydro-2'-deoxyguanosine (8-oxo-dG) is one of the predominant forms of free radical-induced oxidative lesions, and has therefore been widely used as a biomarker for oxidative stress and carcinogenesis.

Search of a diagnostic and predictive biomarker, for adaptation of treatment under the each person and for the best understanding of complex interaction between various pathogenetic mechanisms is one of the major tasks in the modern medicine.

For quantitative analysis 8-oxo-dG isolated from biological samples (blood, brain, urine etc.) is widely used the method of high-performance liquid chromatography (HPLC) with electrochemical detection (ECD) [1]. The HPLC-ECD method allows to detect an amount of this biomarker accurate within 10^{-12} mole.

Increases in 8-oxo-dG levels have been implicated in number of disorders, including cancer, neurodegenerative diseases, atherosclerosis and aging. In our laboratory were realized investigations of the oxidative status and check of medicines' effects on models: experimental hemorrhagic stroke at rates and cirrhosis caused by tetrachlormethane at mouse as also assessment oxidative DNA damage at vitiligo patients and healthy donors [2].

The data obtained during experimental work confirm possibility of using 8-oxo-dG as criterion for monitoring of a course of a disease and also for an efficiency assessment course of treatment.

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DEVELOPMENT OF LIQUID SAMPLE PREPARATION TECHNIQUE FOR ANALYSIS BY ACCELERATOR MASS SPECTROMETER

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The use of radioactive labels is a routine method of drug metabolism and pharmacokinetics investigation. This approach allows defining of drug metabolites or organs they retain in [1]. A significant part of these experiments is radiotracer quantification. For this purpose mass spectrometry (MS) for long-lived isotopes or decay counting methods for short-lived isotopes can be applied. Both MS and decay counting methods have certain shortcomings. MS due to its insufficient sensitivity requires a large amount (which is often unreachable) of sample to analyze. Decay counting methods, on the other hand, presume the use of significant amount of short-lived radioactive isotopes, which can lead to undesirable radiochemical reactions.

Accelerator MS (AMS) is an extension of MS by including a tandem accelerator to bring the ions from tens or hundreds of keV to MeV energies. This provides an efficient detection of long-lived isotopes at **part-per-quadrillion** sensitivities with high precision [2].

The use of AMS benefits in many ways. First of all, the drug of interest dose could be reduced not to cause any damage to a subject of an experiment both in chemical and in radiochemical ways. It should be noted that AMS allows using ^{14}C-labeled compounds at very low radioactive level below the environmental one. Average annual human exposure to ionizing radiation preferentially from airborne radon is varied from 2000 to 5000 µSv, as for radiocarbon it is about 12 µSv. Disease diagnostic dose required for AMS analyses constitutes about 0.1 µSv [Ошибка: источник перёкрестной ссылки не найден]. Secondly, the sample size for the analysis could be decreased up to several micrograms. And finally, prolonged studies of metabolism and pharmacokinetics could be carried out by using AMS technique.

Before being analyzed by AMS samples are to be transformed into a certain state. In case of radiocarbon ^{14}C analysis it is a graphite tablet. Traditional liquid sample preparation multistage technique includes drying, combustion, adsorption of liberated carbon dioxide CO_2, evacuation of residue gases, desorption of CO_2, graphitization and pressing. First two steps have some flaws: the loss of volatile substances which may be ^{14}C-labeled ones during the drying, expensive catalysts for combustion and partial oxidation of sulfur compounds, which poison the graphitization catalyst. Also these steps make impossible to prepare solutions with extremely low target compound concentrations for AMS analyses.

In our work a new method of liquid sample preparation was developed to replace drying and combustion stages in traditional scheme. The method consists in total organic compound oxidation to CO_2 (mineralization) by hydrogen peroxide in the presence of iron containing zeolite as a catalyst. The principal part of our work is a use of zeolitic catalyst, which combines high adsorptivity relative to organic substrate and high catalytic activity in hydroxyl radical formation from hydrogen peroxide. Two functions – adsorption of organic substances and hydrogen peroxide decomposition on the same catalyst provide an efficient mineralization of organic substrate as well as that ones at extremely low concentrations. The work presents experimental results on some bioorganic substrates (acetone, ethanol, glucose, urea) mineralization by hydrogen peroxide using Fe-containing ZSM-5 zeolite. The developed method was a component in *Helicobacter pylori* detection in humans by means of AMS using ^{14}C-labeled urea solutions.

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LABORATORY TECHNOLOGY ADVANCES IN ANTICANCER ALKYLGLYCEROLIPID SYNTHESIS

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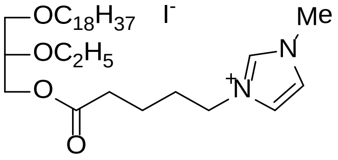
At the present time cationic non-phosphorous ether glycerolipids (CELs) are considered as promising antineoplastic agents which are capable to selectively induce apoptosis of neoplastic cells and to inhibit their entry into normal tissues [1]. It was supposed that CELs can block cancer cell growth by acting on the enzyme-mediated cellular signal transduction processes. In addition to their high antitumor activity CELs possess high elimination half-life and low mutagenicity. The main serious disadvantage of CELs usage as therapeutic agents is their ability to induce hemolysis [2]. Thus, high hemolytic activity of commercially available ether glycerolipid Edelfosine slow down its wide clinical trials.

Cationic lipid – *rac*-*N*-{4-[(3-octadecyloxy-2-ethoxy)propyloxycarbonyl]butyl}-*N′*-methylimidazolium iodide (**1**) – synthesized earlier in our scientific group [3] was found to inhibit tumor cells growth at the same dose concentration as Edelfosine but it did not show any hemolytic activity. To perform advanced biological testing the development of the laboratory synthesis of cationic lipid **1** was carried out in this work.



1

The synthesis of the target lipid **1** includes two main stages: 1) the preparation of a key diglyceride precursor – 1-*O*-octadecyl-2-*O*-ethyl-*rac*-glycerol, and 2) the introduction of the spacer and a cationic group into diglyceride molecule. For the synthesis of diglyceride we attempted a traditional six-step approach based on the initial reagent *rac*-glycerol. Also new short four-step synthetic scheme was elaborated based on *rac*-glycidol. It was found that the yield of diglyceride was 1.8 times lower than in case of the second synthetic route. To prepare cationic lipid **1** the successive introduction of both spacer and cationic head-group also was carried out.

Thus, we were able to reduce the number of synthetic steps and to increase the overall yield of target lipid from 9% to 33%. The realization of our modified technology will make cationic glycerolipid **1** more accessible for wide and extended biological *in vitro* and *in vivo* investigations.

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INNOVATIONS IN PREPARATIVE PROCESSES OF BIOLOGICALLY ACTIVE SUBSTANCES PURIFICATION

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It is clear that development of pharmaceutical industries and biotechnology generates the need for more and more powerful preparative purification methods. When purifying a target biologically active substance (BAS) by preparative liquid chromatography, the objective is to choose conditions and materials that maximize the difference between the migration of this substance and all others in the sample. The amount of product recovered per unit time and the cost involved determine the efficiency of the chromatographic separations. In the frontal displacement chromatography (FDC) one can to reach significantly higher concentration of target biologically active substance (BAS) that possible in linear elution mode under otherwise comparable conditions.

One of the ways for performing the fine separation of BAS by the FDC technique on a preparative or industrial scale is to use quasiequlibrium modes of operation, for which laws of equilibrium sorption dynamics hold.

Using thermodynamic inequalities of sorption quasiequilibrium dynamics, criterion relationships have been derived which determine the formation of a broad chromatographic zone with sharp boundaries of BAS to be separated. The relationships obtained are the necessary and sufficient conditions for the "parallel transfer" regime. On attaining the displacer critical concentration corresponding to be criterion relationships obtained one can observe a sharp broadening of the chromatographic zone of the target BAS and its self - sharpening.

The economic expediency of preparative processes requires the maximal increase in the rate of the mobile phase flow through the chromatographic bed in the experiment. The amount of product recovered per unit time and the cost involved determine the efficiency of the chromatographic separations. In quasiequilibrium conditions for slow diffusing and labile BAS the high efficiency is very hard to reach.

However, study of FDC nonequilibrium dynamics has shown an opportunity of an effective application of nonequilibrium modes for preparative chromatography. It is necessary to use the phenomenon of outlet inversion of components. In the irregular dynamic sorption modes, the very unusual processes in the chromatography when the component with a lower distribution constant appears at the column outlet after the second one can be realized. This inversion of the elution order of the chromatographic bands is due to the effect referred to as "kinetic selectivity" of sorption. The effect arises in dynamic systems at certain combinations of equilibrium and kinetic parameters of sorption.

The output quasiequilibrium and nonequilibrium FDC – diagrams of separation of antibiotics, enzymes and peptides are analysed.

The cost of the tecnological processes is greatly decreased as compared to that of conventional preparative chromatographic processes. Superpure (levels of purification more than 98–99%) BAS were obtained on the use of proposed methods.

The work is supported by the Russian Foundation for Basic Research (RFBR) No. 13-03-00445.

SYNTHESIS OF HETEROCYCLIC SYSTEMS BASED ON CARBONYL DERIVANTS OF DIPHENYL OXIDE

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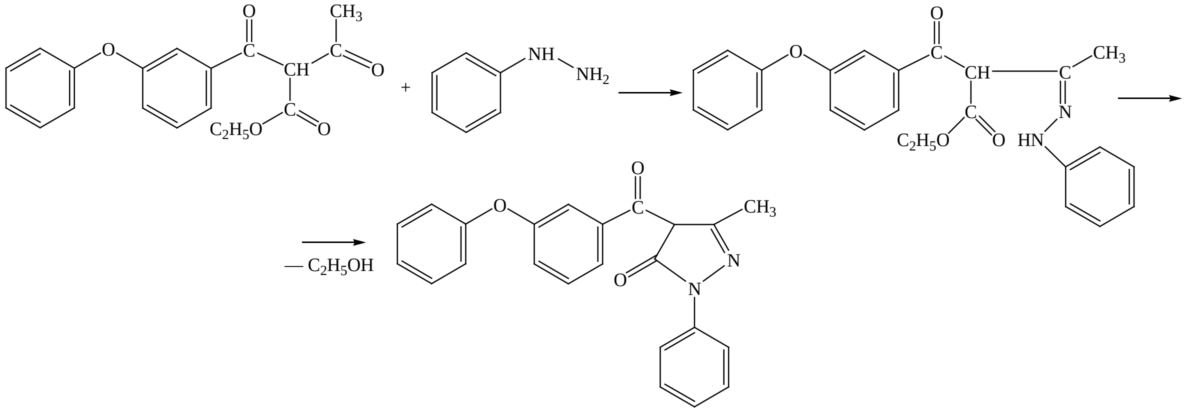
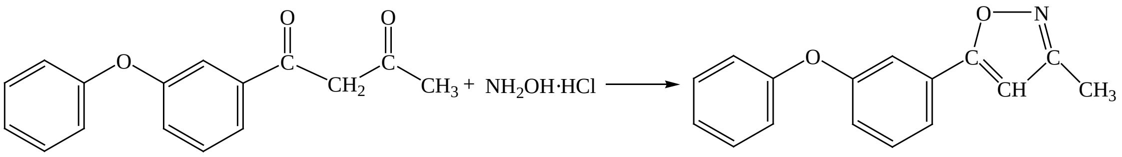
Directed synthesis of heterocyclic compounds with pyrazolone and izoxazole rings, containing a 3-phenoxyphelyl fragment, is the perspective way of obtaining new reactive synthones, allowing to get high performance and low-toxiferous biologically active substances, to expand the range of products and intermediates of fine organic synthesis.

Based on earlier synthesized 3-phenoxybenzoyl acetoacetate [1] and phenylhydrazine we obtained 3-methyl-1-phenyl-4-(3-phenoxybenzoyl)-5-pirazolone:



Synthesis was carried out for one hour at 100 °C at equimolar ratio of reagents in the presence of acetic acid. The reaction mechanism was confirmed by computer calculation of partial charges on the oxygen atoms of the carbonyl groups.

5-Methyl-3-(-3-phenoxyphenyl)isoxazole was obtained by condensation of 1-(3-phenoxyphenyl)butane-1,3-diole with hydroxylamine hydrochloride:



Interaction of reagents was carried out in ethanol (t = 78 °C) at molar ratio 1-(3-phenoxyphenyl)butane-1,3-diole : hydroxylamine hydrochloride = 1 : 2 for eight hours.

According to the computer screening performed using the software complex “PASS Pro 2007 version 3.07” 3-methyl-1-phenyl-4-(3-phenoxybenzoyl)5-pirazolone exhibits potentially high analgesic and antipyretic properties; 5-methyl-3-(3-phenoxyphenyl)isoxazole shows high antiinflammatory and immuno-stimulating properties.

This work was supported by the Ministry of Education and Science of the Russian Federation as a base part of the State task 2014/16, project 2879.

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OPTIMIZATION OF EXCIPIENTS COMPOSITION F OR PARANTERAL EMULSION OF CARBAMAZEPINE

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Carbamazepine (CBZ), 5H-dibenz(b,f)asepine-5-carboxamide is one of the widely used drugs in medical practice for the treatment of patients with epilepsy. However, very poor water solubility of drug (0.061 mg/ml) leads to its slow absorption from the gastrointestinal tract [1], which significantly reduces bioavailability and the overall effectiveness of therapy. Also still there is no dosage form of CBZ for parenteral administration, which is extremely important in emergency assistance in case such as coma, swallowing problems and others. In this regard there is a very actual problem to obtaining a water-soluble CBZ formulation. One of the most suitable solutions to solve this problem is to create a different kind of emulsions. Emulsion formulations offer an appealing alternative for the administration of poorly water soluble drugs due to their effectiveness for drug solubilization, potential for improved efficacy and anticipated patient acceptance and compliance due to the reduced side effects [2]. At present time there is an urgent problem in choosing the conditions for the simultaneous achievement of stability and inclusion of a high percentage of drug in the emulsion.

This study was directed to obtain a CBZ nanoemulsion for intravenous administration which consist of medium-chain triglycerides (Myritol) used as oil phase and Tween 80 as emulsifier. The spontaneous emulsification method this additional sonication was used to prepare different formulation containing 0.5 mg/ml CBZ. The nanoemulsions were evaluated concerning droplet size, zeta potential and drug content.

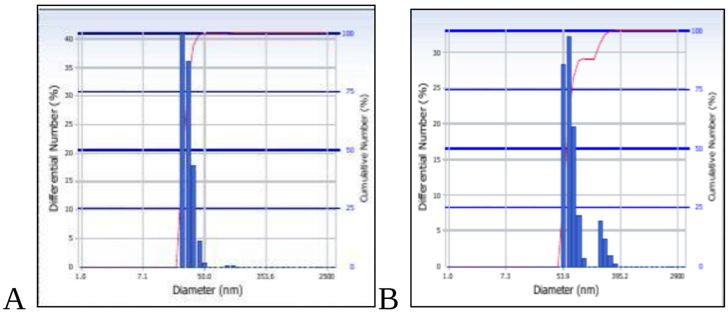

Fig. 1 Particle size distribution in CBZ emulsions: (A) Myritol - Tween 80 (1:1, w/w) and (B) Myritol - Tween 80 (1:1.5, w/w)

The formulation, which presented the best stability properties was selected and refined with respect to emulsifier content. The ratios of oil to emulsifier (Myritol/Tween 80) for the formulations with the greatest stability was 1:1 and 1:1.5 respectively. The particle size of the oil droplets in these samples ranged from 100 to 200 nm. In figure 1 shows the size of the particles of the sample containing Myritol and Tween 80 in a ratio 1:1 (A) and 1:1.5 (B).

Thus, the method was optimized for preparing a stable form CBZ nanoemulsions. It was found optimal percentage of excipients necessary to stabilize the emulsion form.

The results have been obtained within the framework of State task of the Ministry of Education and Science of the Russian Federation.

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THE RESEARCH OF CONVERGENT SYNTHETIC ROUTES TO NEGATIVELY CHARGED FMOC-MONOMERS OF POLYAMIDE NUCLEIC ACIDS MIMICS

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The process of specific interaction of DNA and RNA with natural nucleic acids and their synthetic analogues and mimics is used in many of biomedical technologies. Peptide nucleic acids (PNAs) are presented a functional analogues (mimics) of DNA, in which the sugar-phosphate backbone is replaced by a pseudopeptide. The replacement enables to resist to enzymatic hydrolysis, to be sensitive to the mismatch base pairing etc. PNA monomer unit can be modified by known methods. Previously, our research group has been synthesized the PNAs oligomers derived from L-Glu by solid phase synthesis (SPS), it has been demonstrated that these substances form complexes with complementary targets. However, Boc-protocol has not appeared to be effective due to the fact that the highly acidic conditions of cleavage of the target oligomer from the resin lead to its decomposition, so it seems appropriate to develop Fmoc-protocol SPS to modify PNA based on L-Glu.

PNA monomers can be prepared by various routes (see Fig. 1). The first approach using Mitsunobu reaction have performed well, in case of the preparation of monomers for Boc-protocol. Since the Fmoc-group is unstable under thiolysis conditions, we used as a starting compound Cbz-protected alcohol (3). N-Cbz-protected monomer (4) was prepared by known procedures. Unfortunately, the attempts to convert the Cbz-monomer (4) to Fmoc-monomer (8) were unsuccessful due to the formation of the cyclic side product (6). So, currently the modification of this approach to use (trimethylsilyl)ethyl group as the C-terminus is developed.

Also, the alternative experiments were carried out on synthesis of aldehyde (7) and subsequent reductive N-alkylation of a glycine derivative (9), but the yields and reproducibility of these techniques appeared unsatisfactory. We attribute this to a lack of studying of conditions of the alcohol oxidation to aldehyde (temperature and reaction time, choice of oxidant).

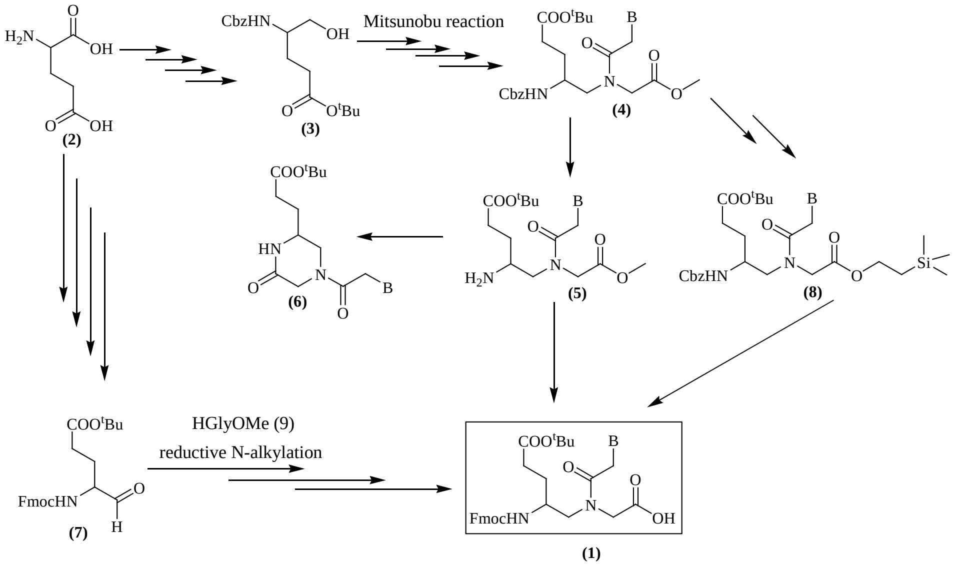

Figure 1. Scheme of the synthetic routes for the producing of Fmoc-PNA monomers.

Thus, we have tried out several routes of synthesis of Fmoc-PNA monomers derived from L-Glu and found the solutions for a number of difficulties encountered in the implementation of these approaches.

The work was performed as part of the State task of the Ministry of Education and Science of the Russian Federation (proiect No. 4.128.2014/K).

DIMERIC POLYCATIONIC AMPHIPHILES AS PROMISING GENE CARRIERS

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Gene therapy is the trend of modern medicine focused on the treatment of hereditary or acquired diseases caused by gene defects (mutations). The main idea of this method is to provide the delivery of properly acting gene copy or antisense gene construction into the site of the defect resulting in the replacement or blocking of adverse gene. Cationic liposomes are promising gene carriers which are capable to transfer various types of nucleic acids and gene constructions into cells. Formed from positively charged amphiphiles cationic liposomes bind and condense nucleic acids and protect them from extracellular degradation. Moreover they possess a number of advantages namely low immunogenicity, low-costing and large-scale production opportunities.

We have found earlier that liposomes consisting of spermine-based dimeric amphiphiles having two cholesterol or diglycerol moieties were able to transfer pDNA, RNA and siRNA into eukaryotic cells with the efficiency superior to those of commercial reagents.

To improve nucleic acid delivery we have synthesized a number of spermine containing amphiphiles and their triethylentetramine analogues bearing disulfide or acetal linkers. It is known that disulfides and acid-labile compounds could be destroyed in the presence of intracellular reducing agents or during endosomal acidification. Due to these properties the presence of these kinds of linker groups will prevent the extracellular liberation of nucleic acid from liposomal complexes and will provide better releasing it after cellular uptake.

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THERAPEUTIC AND PROPHYLACTIC BATH SALTS WITH ADDITION OF IRON BIOLOGICALLY ACTIVE COMPOUNDS

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Recent years, doctors often suggest to use to relieve fatigue, stress, allergies and various flavored medicated bath salts. Demand salts of various mineral springs and iodized sodium chloride [1].

Effectiveness of water treatment depends on the composition and water conditions, as well as the interaction of living cells with it. The presence of different substances in the water, changing its electrical conductivity, leads to a change in metabolism in the living cell. When this enhanced or inhibited by the course of biochemical reactions and the overall behavior of the cells is fully dependent on an external osmotic pressure composition that is created of ions and water molecules undissociated.

Using a salt reduces the physiologically important intracellular ratio of the elements K^+/Na^+ and reduces the total concentration of other, equally important ions (Ca^{2+}, Mg^{2+}), disrupting the functioning of cellular systems. Therefore salt compositions for baths with additives of various biologically active substances, plant extracts [2] are more effective. We have developed 4 types of salt for therapeutic baths with extracts of local plants: basil, peppermint, rose petals and fruit of juniper berries (sources of macro-and micronutrients, vitamins) as well as biologically active coordination compounds of iron with anions of acetic, succinic, salicylic and citric acid. Heterovalent iron coordination compounds with anions derived acids mentioned under nitrogen flow (under argon). Synthesis of complex is carried out at pH 5.5–6.0, the ratio Fe(III): Fe(II) 1:1, and a slight excess of said acid at a temperature of 50–60^{o}C in the pH range from 4.0 to 5.5.

The main component of the therapeutic and prophylactic composition is pure iodized salt Gissar deposits of Republic of Tajikistan [3]. The final product is prepared by mixing sodium chloride with one of the types of the extract, such as basil and heterovalent iron complex with ligands of citric acid.

Composition of plant extracts rich in essential oils, glycosides, saponins, tannins and minerals, vitamin C and A, carotene, volatile production, vegetable fats and simple sugars. The contents of all macro-and micronutrients, many vitamins promotes intracellular ratio of elements and ensures the normal functioning of cellular systems. The coordination compound of iron and facilitates the transport of oxygen promotes oxidation-reduction reaction, treatment and preventive improves efficiency and increases the specific activity of the salt components.

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RESEARCH OF CATALYTIC HYDROGENATION OF NITROBENZENE IN SUPERCRITICAL CARBON DIOXIDE

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Catalytic hydrogenation of a nitrobenzene is important chemical and technological process of receiving aniline which is in turn used as intermediate in synthesis of polyurethanes, rubbers, pharmaceuticals, pesticides and herbicides. Process of gas-phase hydrogenation of a nitrobenzene is usually carried out with use of Ni-or Cu-containing catalysts, fractional pressure of hydrogen of 1–5 atm. and temperature 250–300°C, while liquid-phase hydrogenation – with use of Pt-, Pd-, Ni-containing catalysts at a temperature of 50–220°C and pressure of 10–50 atm. both in the environment of various solvents, and in their absence, thus selectivity on a main product makes 75–95% [1].

Application of supercritical carbon dioxide in selective hydrogenation of a nitrobenzene has the considerable interest of researchers that is caused by advantages supercritical fluids application: high heat and mass transfer, formation of new molecular complexes and decrease of processes flammability.

Nitrobenzene hydrogenation in supercritical carbon dioxide was carried out in the following conditions – temperature of reaction 90°C, mass of a nitrobenzene of 2.4 g, mass of the catalyst of 0.1 g, partial pressure of hydrogen 50 atm, partial pressure of carbon dioxide of 200 atm.

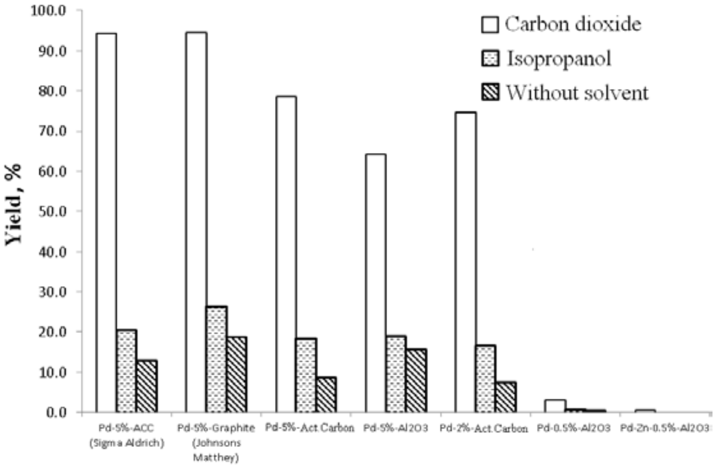

Fig 1. Screening of activity of the studied catalysts in the environment of supercritical carbon dioxide, isopropanol and without solvent.

On the basis of the obtained data presented in figure 1, it is possible to see the increase of reaction rate of aniline formation in 3.5-5 times in case of supercritical carbon dioxide application compare to conventional solvent – isopropanol and reaction without solvent.

During the analysis of reaction liquid a main product of reaction – aniline, and the intermediate products of reaction were found, including: nitrosobenzene, phinilhydroxylamin, azoxybenzene, azobenzene, hydrazo-benzene. The highest yield of aniline was found to be 95%.

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ENANTIOSELECTIVE SYNTHESIS OF A KEY INTERMEDIATE IN A NEW PROCESS FOR GABA ANALOGS USING NI(II)-CATALYZED MICHAEL ADDITION

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γ-Aminobutyric acid (GABA) is the major inhibitory neurotransmitter in the central nervous system. Addition of malonates and 2-oxophosphonates to nitroalkenes is good approach to the key precursors of GABA-derived drugs [(*R*)-fenotropil, (*R*)-baclofen, (*R*)-phenibut, (*R*)-rolipram, (*S*)-pregabalin] and chiral substituted γ-aminophosphonic acids – a potent GABAergic compounds.

Except anticonvulsant (*S*)-pregabalin these drugs were commercialized in its racemic forms, it has been reported that its biological activity resides exclusively in (*R*)-enantiomer of aryl GABA derivatives. Use of non-racemic pharmaceutical substances will allow to lower a dosage of drugs and to increase efficiency of nervous diseases therapy.

There are many methods available in the literature on the synthesis of enantiomerically pure GABA derivatives. They are concerned mostly with resolution, chemoenzymatic, or use of chiral auxiliary. However, these methods suffer from disadvantages such as the low overall yields, the need of separation of precursor diastereoisomers and the use of expensive chiral reagents in stochiometric amounts. In this context, a more performance approach for the synthesis of enantiomerically pure GABA derivatives and analogs is highly desirable.

Herein we report the efficient atom-economic technology of the synthesis of GABA analogs on the basis of transition metal catalyzed asymmetric Michael addition.

Enantioselectivity of the addition of diethyl malonate, 2-oxophosphonates and 2-oxosulfoxides to nitroalkenes were investigated in the presence of transition metals complexes (Ni, Co, Mn, Fe, Cu) with chiral nitrogen-containig ligands (substituted *trans*-cyclohexane-1,2-diamines, *L*-proline and (*S*)-camphor derivatives).

Catalytic activity of transition metal complexes decreases in this order:

$$\mathrm{Ni} > \mathrm{Mn} > \mathrm{Co} > \mathrm{Fe} > \mathrm{Cu}$$

Enantioselectivity of reaction in the presence of transition metal complexes decreases in this order:

$$\mathrm{Ni} > \mathrm{Co} > \mathrm{Mn} > \mathrm{Cu} > \mathrm{Fe}$$

The complex Ni(II)-bis[(*R*,*R*)-N,Nr-dibenzylcyclohexane-1,2-diamine]Br_2 showed the greatest catalytic activity.

We showed that activation by Et_3N of a Ni(II) complexes with one chiral diamine ligand is possible. It gives the chance to reduce quantity of a chiral ligand.

As result we have developed performance catalytic system with minimal content of chiral component, which provide high yield of the Michael adducts and 92–99% *ee* at concentration of the catalyst 0.2 mol. %.

Hydrogenation of the chiral adducts of malonates and nitroalkenes and hydrolysis of the formed pyrrolidine-2-one-3-carboxylates leads to 3-substituted GABA.

Obtained catalysts were successfully used for development of the production process of non-racemic pharmaceutical substances of (*R*)-fenotropil, (*R*)-baclofen, (*R*)-phenibut, (*R*)-rolipram and (*S*)-pregabalin.

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MICROWAVE SYNTHESIS AND X-RAY PHOTOELECTRON SPECTRA OF LANTHANIDE TETRAARYLPORPHYRIN COMPLEXES

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The research activity in the chemistry of lanthanide porphyrin complexes is largely focused on their unique luminescent properties. Of the 15 lanthanides, ytterbium attracts wide research interest due to its near-infrared region luminescence and rather small ionic radius. Ionic radii of the elements decrease in the lanthanide series (lanthanide contraction): Er – 1.03 Å, Yb – 1.01 Å and Lu – 1.00 Å.

Luminescence properties of lanthanides attract much interest related to their potential utility in biology and medicine. Diamagnetic lutetium complexes exhibit weak phosphorescence at 77 K. At the same time, erbium and ytterbium porphyrin complexes show 4f-4f luminescence in the near-infrared region which is excited by intramolecular energy transfer from the porphyrin triplet state to the lower resonance levels of Er(III) and Yb(III) [2].

The aim of our research work was the optimization of synthesis conditions of a number of lanthanide tetraarylporphyrin complexes including a use of microwave radiation; studies of their chemical composition, electronic structure and spectral characteristics. We carried out some experiments with use of microwave radiation, various solvents and their mixes (acetic and propionic acids, nitrobenzene); catalyst, reaction time, temperature and microwave radiation power were also varied.

Results of carried out researches demonstrate the possibility of receiving the lanthanide porphyrin complexes by use of microwave radiation technique [3]. Thus, the time of process is considerably reduced, energy consumptions decreased, reactions are carried out at lower temperatures, there is no need for an inert atmosphere. The X-ray photoemission spectroscopy data show different atomic constituents in accordance with its states in the molecules which can be related to the peaks appearing in the electronic spectra. Different peaks were seen in the C1s spectra are related to the chemically unequivalent C atoms in the molecules. In rare-earth elements metalloporphyrins charge distribution for N is more uniform with single N1s peak at about 399 eV in spectra. Evident multiplet structure in the 4d spectra of Yb, Er and Lu metalloporphyrins clearly indicates the trivalent state of REE in compounds.

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Au-CONTAINED NANOSTRUCTURED CATALYSTS IN SYNTHESIS OF 2-METHYL-1,4-NAPHTHOQUINONE

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Vitamins of K group, or antihaemorhagic vitamins, are necessary for a normal fibrillation. It s applied at strong bleedings, haemorhagic diathesis and in certain cases of a liver functions frustration. Vitamin K_3 (menadione) is a synthetic analog of vitamins of K group.

There are a lot of catalysts described in literature which are applied in the menadione synthesis, however the majority of them gives low selectivity (<40%), is toxic, pollutes the prime product and gives a considerable quantity of by-products [1]. We decided to use the based on HPS catalysts, because of their properties. Hypercrosslinked polystyrene (HPS) is rigid polymeric network of polystyrene linked by methylene bridges. Rigid polymeric matrix of HPS allows stabilizing metal nanoparticles and controlling their growth, due to the presence of nanopores with high degree of monodispersion [2].

At oxidation 2-methylnaphthalene such products, as 2-methyl-1,4-naphthquinone (menadione, the precursor of vitamin К3), isomerous 6-methyl-1,4-naphthquinone, methyl groups oxidation products, dinaphthquinone, epoxiquinone and other products of deep oxidation are formed [1].

At first industrial non-catalytic reaction of 2- methylnaphthalene oxidation by a chromic mix has been in vitro researched. The key product of this reaction is menadione (the vitamin К3 precursor). Oxidation was conducted in the glass reactor within 10 minutes at the temperature from 40 to 90 ^{o}C. Concentration of a 2-methylnaphthalene solution in acetic acid is 1M. Samples were taken every 2 minutes during the reaction and analyzed using GC-MS.

2-Methylnaphthalene catalytic oxidation was carried out with the use of HPS-based Au-catalyst in H_2O_2 presence. Synthesis of such system was carried out by introduction of metal in a carrier by impregnation on a moisture capacity of different salts. The further researches will be directed on a variation of parameters of reaction and structure of catalytic systems.

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TECHNOLOGIC AVAILABLE FERROCENE-BASED COMPOUNDS FOR MEDICINAL APPLICATIONS

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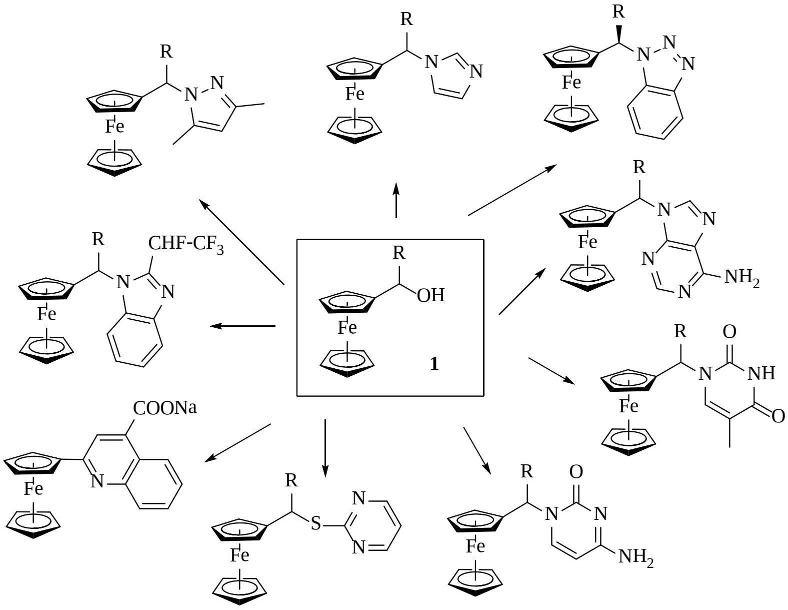
Ferrocene-containing compounds are in demand as objects for medicinal research [1]. A wide range of approaches were developed to prepare different ferrocenes [2]. Accessible initial reagents and technological reaction conditions combined with unique ferrocene properties have made such type compounds very popular. A large number of ferrocene compounds were investigated as potential antianemic, antimicrobial, anticancer drug candidates. However, to date the only drug on the basis of ferrocene it is known. This drug, named ferroceron – *orto*-carboxybenzoyl ferrocene sodium salt, is used for treat anemia and other diseases associated with iron deficiency.



R =H, Me, Et, Ph

The simple and effective routs to ferrocenylalkyl *N*,- *S*-, *F*-containing heterocycles including regioselective and stereochemical aspects will be discussed [2]. Ferrocene-modified biological active compounds on the basis of organic molecules (Scheme, for ferrocene-based hinoline acetylferrocene was used as source reagent) namely, nucleobases, aminoacides, pyrimidines, chinoline, azoles were synthesized in good or quantitative yields from hydroxyalkyl ferrocenes (I). All these processes are technologically available and can be implemented in industry.

This work was supported by the Russian Academy of Sciences (Presidium Program “Fundamental Sciences for Medicine”), by the Department of Chemistry and Materials Science (Program “Medicinal Chemistry”) and by the Russian Foundation for Basic Research (RFBR No 14-03-00980).

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CATALITIC LACTOSE ISOMERISATION

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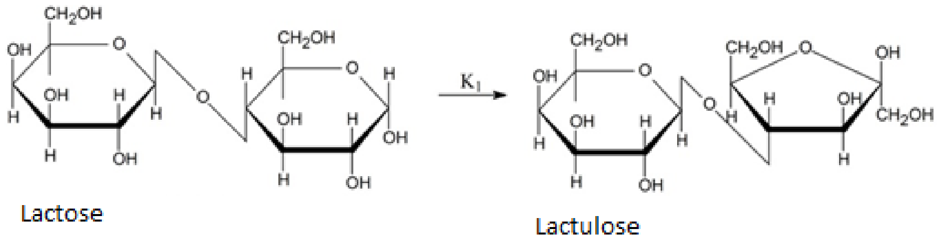
Lactulose is a synthetic ketose disaccharide that has valuable pharmaceutical application. Lactulose has considerable medical interest for the treatment of portal systemic encephalophathy and chronic constipation. It is also used as a Bifidus factor in nutrition and is known to be an important humanizing factor in infant formulas. This sugar has greater sweetness compared to lactose and therefore it can be used in baking and confectionery applications.



To carry out the experiment the solutions of lactose with pre-calculated mass concentration were prepared. The reaction was performed in Parr Series 5000 Multiple Reactor System (six blocks) in a nitrogen atmosphere. While carrying out the experiments such reaction condition as the ratio of the catalyst mass to the mass of lactose taken was varied. During the reaction at given intervals samples were taken, the sample volume was 4 ml.

The reaction was carried out with the catalyst – boric acid supported on magnetic particles. The maximum selectivity was 87% at 70% conversion. The increase in conversion results in considerable decrease of selectivity up to 30–60%. The most conversion 80% was observed in experiment 1 (Fig. 1). The increase in nanoparticles content leads to the increase in conversion and selectivity.

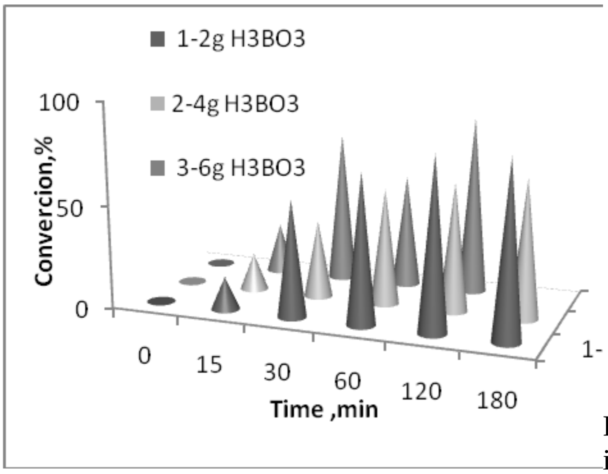


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Fig.1. Conversion dependence on the time in the isomerization of lactose (at 60 ° C, pH 7).

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STUDY OF BIOLOGICALLY ACTIVE SUBSTANCES PRODUCTION PROCESS USING THE EXAMPLE OF INDUSTRIAL TALL OIL PRODUCTS OF DECARBOXYLATION REACTION

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Unsaponifiables (or neutral substances) of tall oil is a group of natural high-molecular weight products which due to the peculiarities of the structure and physical-chemical properties are characterized by high biological activity. The purpose of this work was the study of the extraction process of unsaponifiable substances contained in lignin containing waste products of tall oil, byproducts of wood processing at pulp and paper industry, and confirmation of their biological activity.

At the first stage of research there were developed and proposed the methods of extraction of unsaponifiable matters from crude tall oil. The most promising in terms of quantitative output of biologically active substance from basic lignin containing wastes was the method, which was based on the implementation of the saponification process of all fatty and resin acids of crude tall oil with alkaline solutions of NaOH or KOH, with the subsequent extraction of unsaponifiable matters from soap solutions using appropriate solvents (traditional extraction process). During the works NaOH and KOH solution concentrations, molar ratio with crude tall oil, temperature regimes of process implementation have been chosen and the aspects of the process hardware design have been studied. In the second phase aqueous solutions of fatty and resin acids soaps were treated with various solvents, which later were enriching with unsaponifiables. Within the scope of this stage of works solvents of various hydrocarbon structure have been tested. For the best of them concentration, time and processing temperature were chosen, time and separation temperature of the products after the extraction process were set. Solvent removal and unsaponifiable substances concentration schemes without changing physical-chemical properties of solvent and unsaponifiable substances were proposed.

The second method of extraction of unsaponifiable substances contained in tall oil lignin containing waste was the method of transition of fatty acid components into the appropriate paraffin and olefin hydrocarbons through decarboxylation process. Extraction of required biologically active substances from industrial tall oil decarboxylation products was carried out by the method of cooling and filtering deposited natural unsaponifiable matters in the sediment. Although as far as process design is concerned this method is simpler and more readily available for industrial application than the first one, the losses of biologically active substances in this case exceed 60% from theoretically possible yield.

Estimation of biological activity of unsaponifiable substances was carried out during the tests on germination and sprouting of wheat, as well as by applying traditional methods of determination of biological activity using living organisms.

THE IPSO-SUBSTITUTION IN THE 5,7-DINITRO-8-HYDROXYQUINOLINE

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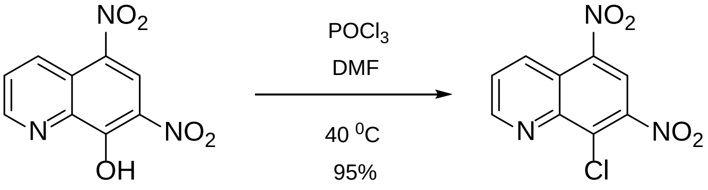
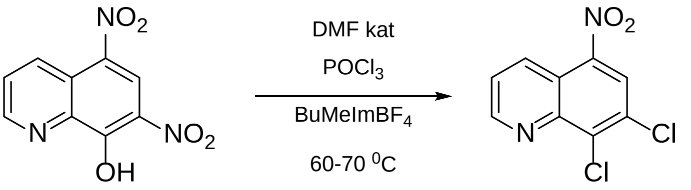
Currently, many studies have shown that ionic liquids are widely applied in different areas of chemistry, including organic synthesis. They act as catalysts and as the organic solvents in the reactions. So, the effect of the ionic liquid on the nitration of aromatic substrates was described in works [1], [2].

We have studied previously described in the literature reaction (1) - hydroxy substitution in the 5,7-dinitro-8-hydroxyquinoline by one chloro $POCl_3$ in DMF - using an ionic liquid as a solvent (2):



1 2 (1)



1 3 (2)

To a suspension of 5,7-dinitro-8-hydroxyquinoline **1** in $BuMeImBF_4$, under vigorous stirring, was added a 1,2-fold excess of phosphorus oxychloride, and a catalytic amount of dimethylformamide. The mixture was heated at 70^0C for 2 hours. After diluting the reaction mixture with water a precipitate was filtered. Methods of molecular spectroscopy was found that during this reaction was first obtained 7,8-dichloro-5-nitroquinoline **3**, the product of substitution of the hydroxyl and nitro. The yield of the obtained compounds was 95%.

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THE SELECTIVE REDUCTION OF THE NITRO GROUP IN 5,7-DINITRO-8-HYDROXYQUINOLINE

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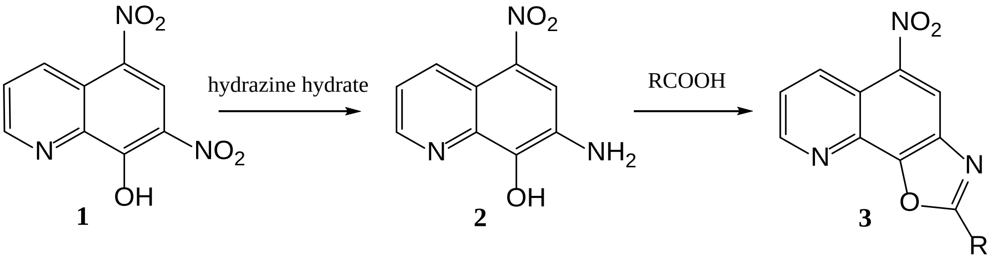
Theoretical and practical interest to compounds containing benzoxazole fragment due to their diverse biological activity. These include oxazoloquinolines [1], [2].

In connection with this, we first conducted synthesis of 7-amino-5-nitro-8-hydroxyquinoline **2** in the presence of hydrazine hydrate:



1 **2** **3**

Weigh the original 5,7-dinitro-8-hydroxyquinoline suspended in a small amount of water. Further, the reaction system was added hydrazine hydrate calculated and maintained under heating during the day. After one day, a precipitate of light yellow color, which is filtered and washed with water. The structure of the resulting 7-amino-5-nitro-8-hydroxyquinoline was proved by molecular spectroscopy.

Compound **2** is a novel starting material for the synthesis of oxazoloquinolines **3** by cyclization with carboxylic acids.

After the restoration of the remainder of the nitro group to provide additional fragments associated with the nitrogen atom - azocompounds, amides. This will provide a wide range of materials to study their properties.

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ABOUT COEFFICIENTS OF THE CONVECTIVE HEAT EXCHANGE FROM THE HEATING WALL TO THE PULSING LAYER OF DISPERSE MATERIALS

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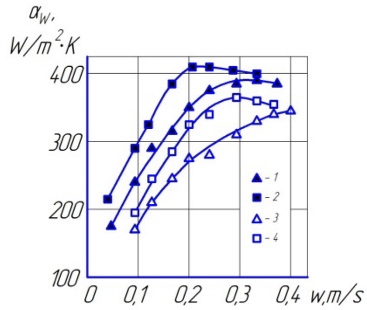
The use of a pulsing layer technics for drying of badly loose pharmaceutical materials allows not only to stabilize a hydrodynamic regime of their processing, to expel a channel formation, presence of stagnation zones at simultaneous decrease dust ablation, but also considerably to intensify heat exchange between a layer and the heating surfaces placed in it [1–3].



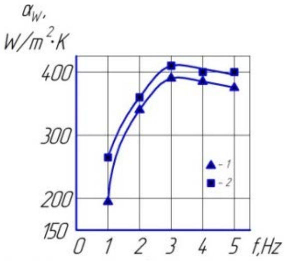
1-MAA, f=3 Hz; 2-aminalon, f=3 Hz;
3-MAA, f=0 Hz; 4-aminalon, f=0 Hz

Fig. 1 – Dependence of coefficients of convective heat exchange α_{CT} from air speed w at processing of MAA and aminalon

We spend an experimental estimation of a convective heat exchange coefficients from a heating wall to a pulsing layer of air-dry medical ascorbic acid (MAA) and gamma-aminobutyric acid (aminalon), and also agency on it of fluidization agent velocity w and a pulsation frequency f is revealed.

Regime parameters of process varied over the range: w=0,04–0,4 m/s, f=1–5 Hz at porosity of a pulse ψ=0,5. In the capacity of fluidization agent the air was used. Comparative experiments according to magnitude of a convective heat exchange coefficients from a heating wall to a fluidized bed of investigated materials are executed.

It is established (fig.1), that character of dependence $\alpha_W=\varphi(w)$ is identical both for a pulsing layer, and for usual fluidized bed. However, the maximum values α_W for a pulsing layer on the average on 10–12% more and also are reached at velocity of air on 20–30% smaller, than in fluidizing layer. With increase of pulsation frequency (fig.2) values α_W with other things being equal also increase, and their maximum values correspond to the condition of a layer characterized by minimum porosity (a piston regime).



1-MAA, w=0,28 m/s; 2-aminalon, w=0,2 m/s

Fig. 2 – Dependence of coefficients of convective heat exchange α_{CT} from a pulsation frequency f at processing of MAA and aminalon

The obtained data can be useful to a substantiation of optimum operating modes of drying apparatuses with a pulsing layer and the combined heat input.

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DEVELOPMENT OF GENETIC CONSTRUCTS FOR GENERATION OF ADALIMUMAB EXPRESSING CHO CELL LINE

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Recombinant monoclonal antibodies (rMABs) are widely used biopharmaceuticals, normally produced in genetically modified Chinese hamster ovary cells (CHO). Adalimumab is a human MAB against tumor necrosis factor alpha used to treat different autoimmune diseases. Generation of highly productive CHO cell lines should be the primary aim for the development of rMAB upstream process.

Aim of the study is creating genetic constructs for the following transient and stable transfection of CHO cell line to obtain adalimumab with the highest possible yield.

The genes encoding heavy (HC) and light chains (LC) of adalimumab were synthetic, optimized for expression in rodents. Expression constructs containing HC and LC genes and a selection marker DHFR were obtained on the basis of pOptiVEC and pcDNA vectors, as well as tricistronic vector pOptiVEC-TOPO-IRES FMDV. Transient transfection of CHO-DG44 cells was performed using Freestyle MAX reagent (Invitrogen). Selection of positive clones was performed by limiting dilutions. Expression of both chains was measured by ELISA of cell culture supernatants.

Genetic constructs for CHO-DG44 cells transient and stable transfection to obtain MAB adalimumab have been developed. The results suggested that maximal transient expression was achieved by using separate plasmids. The highest expression levels in transient transfection were obtained with the use of pOptiVEC-HC and pcDNA-LC plasmids combination. The stability of antibody expression and heavy/light chain ratios in the best expressing cell lines will be further analyzed in the cell culture.

THE ISOSTERIC 1,2,4-TRIAZOLE-3-CARBOXAMIDE ANALOGUES SYNTHESIS: OXADIAZOLE AND TRIAZOLE DERIVATIVES

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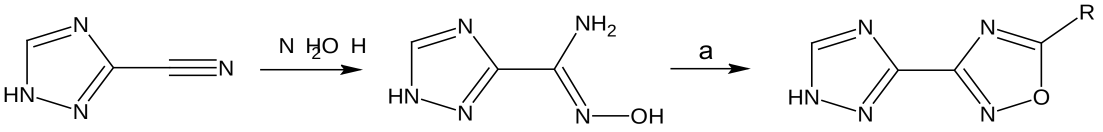
1,2,4-Triazole-3-carboxamide (heterocyclic base of the ribavirin molecule) conformationally mimics the purine base moiety of natural nucleosides: guanosine , inosine and adenosine. It is a view that for this reason the ribavirin 5' -phosphate derivatives effectively inhibit viral enzymes such as inosine monophosphate dehydrogenase, RNA polymerase, guanyl transferase and etc., thus disrupting the process of viral replication in the cell.

The first stage of ribavirin cell metabolism is phosphorylation by nucleoside phosphorylases (PNP). 1,2,4-triazole-3-carboxamide (TCA) is a purine nucleoside phosphorylases substrate in the transglycosylation also that is replacement of the nucleoside heterocyclic base. Recently we have found a bulky substituent in the amide group containing TCA analogs are also substrates of PNP [1] but there are not conformationally similar to the purine molecules. It turned, presence of carboxamide group is not necessarily. We have proved that 5-methyl-(1H-1,2,4-triazol-3-yl)-1,2,4-oxadiazole (TCA analogue) is a PNP substrate wherein carboxamide group is replaced by isosteric oxadiazole group.

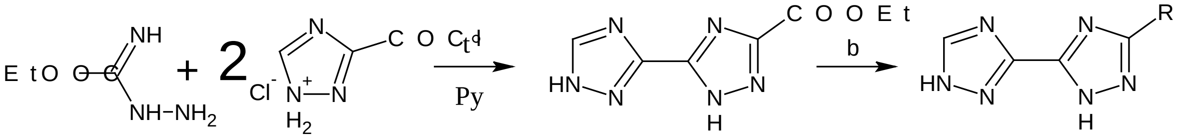
The goal of this work was a number of isosteric to carboxamide group heterocyclic (triazolyl, oxazolyl, imidazolyl and etc.) substituents containing TCA analogues to obtain.

Synthesis of analogues TCA containing 1,2,4-oxadiazole moiety performed according to the following scheme:



R = H, a: $HC(OEt)_3$, t°; R = CH_3, a: Ac_2O, AcOH, t°; R = C_6H_5, a: 1) RCOCl, Et_3N, 2) TBAF

In a continuation our work [2] we synthesized analogues TCA containing 1,2,4-triazole moiety:



R' = H, $H_2SO_4:H_2O$ 1:4, t°; R' = COOH, b: NaOH, EtOH, H_2O; b: NH_3, MeOH, R' = CON

Structure of the synthesized compounds are confirmed by physicochemical methods.

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NATURAL PECTINS AS PERSPECTIVE POLYMER CARRIERS OF MEDICAL PRODUCTS

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Natural polysaccarchides pectins have wide applications in various branches of industry that is due to its wide distribution in natural vegetation, low toxicity and biological activity. An additional interest to the pectins is stimulated by the possibility of employing original pectins or its oxidized fractions as polymer base while creating new medical forms with a controled release of pharmacologically active matters. In view of this, the aim of the present work is to study the oxidative descrtuction of pectins (P) in reaction systems «P + H_2O_2 + O_2 + H_2O» and «P + O_3 + O_2 + H_2O» and their reaction with some nitrogen-containing compounds.

As the object of study we choose citrous and apple pectins with molecular masses 162 kDa and 213 kDa respectively. As nitrogen-containing compounds we employ 4-, 5-aminosalicylic acids and uracil with a series of its derivatives (5-fluorouracil, 6-methyluracil, 5-amino-6-methyluracil, 5-bormine-6-methyluracil, 5-hydorxy-6-methyluracil, 5-nitro-6-methyluracil). As the dissolvent, a fresh-made bidistilled water served.

The pectins dissolved in water were oxidized by the hydrogen peroxide (or ozon-oxygen mixture) in a glass constant-temperature reactor of bubble type and the samples are periodically taken. The concentration of carboxyl groups were determined by potentiometric titration. Once the reactions was over, the oxidized polysaccharides fractions were sorted out by acetone deposition under the volume relation of the reaction mixture and acetone 1:2. The characteristic viscousity of pectins solutions were measured in Ubbelohde viscometer with hanging level. The molecular masses of original polysaccharides and of their oxidized fractions were calculated by the characteristic viscousity with employing Kuhn–Mark–Houwink–Sakurada equation.

Oxidizing and desctructive transformations of pectins in reaction systems «P + H_2O_2 + O_2 + H_2O» and «P + O_3 + O_2 + H_2O» are justified by the data on changing viscousities for water solutions of polysaccharides. For both reaction systems we have studied the influence of initial conditions (the oxidation time, the temperature and the concentratin of oxidants) on the process of oxidatin functionalization and destruction of citrus and apple pectins. On the basis of obtained results we have found the conditions for obtaining oxidized fractions of studied pectins with prescribed molecular masses.

It is established that addiing of the original pectins or their oxidized fractions to water solutions of nitrogen-containing compounds leads to hypsocromic shifts and changes in the intensivities of absorbtion maxima in UV spectra of aminosalicylic acids and uracils. These changes can be considered as the results of intermolecular interactions occruing in reaction systems «pectins (oxidized fractions of pectins) + aminosalicylic acids (uracils)» and leading to creation of complexes. The structure of complexes determined by the methods of isomolar series and molar quotients happens to be 1:1 in all the cases. We calculate the stability constants for created compounds. Studying the influence of substitutors nature in the molecul of 6-methyluracil on the complexes stability shows that introducing electron-donor substitutors in the fifth position of 6-methyluracil molecules stimulare the stability increasing for created complexes.

The work is supported by a grant of the Russian Foundation for Basic Research (project 14-03-97026-r_povolzhe_a) and the project (No. 1007, 2014.) performed by the university within the basic part of the State task of the Ministry of Education and Science of the Russian Federation.

Section 4

Technology of Obtaining Inorganic Materials

THE INFLUENCE OF ORIENTATION OF SILICON SUBSTRATE AND CONCENTRATION OF SHALLOW DONORS ON MECHANISM OF NANOPOROUS SILICON FORMATION

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The fact of porous silicon (PS) formation when etched in HF acid solutions with applying the current flow was first described in 1956. The most widespread method of porous silicon layers formation is anodic etching of the silicon substrate in the solutions contained HF and H_2O or/and C_2H_5OH.

Nowadays there are a lot of theories using of which scientists try to explain the process of PS formation. In most cases these models consider the chemical aspect of the interaction between single-crystal silicon and HF acid. At the same time the questions connected with the initial genesis centers have not exact explanation. In general, the majority of scientists see them as random processes linked with different surface defects. But that consideration makes great uncertainty in this subject. The other important item is that the F^- ion is assumed as the main reaction unit; however, it isn’t an unmistakable fact.

We have carried out a series of experiments to investigate the influence of various factors of the surface condition on the result porous layers. In particular we have researched these influences on the pore’s diameter, since it is joined straight to the initial genesis centers. The concentration of the shallow donors (for example B or P) was found out to affect the pore diameter and the layer thickness. The thickness of porous layers was established to be limited to the value 45–50 μm on p-type wafers and 250–270 μm on n-type wafers.

The surface morphology research of PS using the scanning electron microscope shows that the contour of the pores of the investigated structures tends to the square shape. According to our opinion, that could be explained, if to suggest that the HF_2^- ion is the main reaction unit in the electrochemical process.

The HF_2^- ion is well known from the literature data to have the almost linear structure. The size of the ion HF_2^- together with the bond distance of Si-F corresponds to the lattice constant of single-crystal Si. It helps to understand the reasons of the slope of the porous silicon layers on the samples orientated in the direction <111>.

The results have been obtained within the framework of State task of the Ministry of Education and Science of the Russian Federation.

ANALYSIS OF A PROCESS OF RUTILE CONCENTRATE FLUORINATION

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A scientific research reveals gaps in existing industrial technologies of titanium production. A need for development of a new technology of processing of titaniferous concentrates was justified in the research. With the use of “ASTRA” software, a thermodynamic research of the process of rutile concentrate fluorination by elemental fluorine was conducted. The abovementioned research showed that the process had no restrictions from the thermodynamic point of view. Kinetic characteristics of the process were investigated, and results were mathematically treated. It was established that the process was limited by diffusive factors, such as supply of fluorinating reagent to a solid surface. Energy quantity needed for fluorination process activation was determined. The research provides conditions of process realization in production environment.

At the present time, there are two ways of processing of titaniferous concentrates. They are based on use of either sulphuric acid or chloride. The sulphuric acid technology is connected with environmental pollution; and the cost of produced titanium dioxide is high. The chloride method is considered to be more favorable for the environment. However, the method is also connected with formation of large amounts of gaseous, liquid and solid chloride-containing industrial wastes [1]. World production of 2,750 thousand tons of pigment titanium dioxide per year leads to formation of 1,467 thousand tons (4,890 tons per a day) of hazardous chlorine industrial solid wastes per year (upon condition that all plants use chloride method) [2].

If intermediate fluorides are formed from TiO_2, the process speed is high; and fluorine may be used almost completely. The counterflow process of titanium tetrafluoride production from intermediate fluorides consists in feed of fresh fluorine to process partially fluorinated product, and flue gases are used to process fresh titanium dioxide [1]. In static conditions (or at insufficient mixing intensity) and if fluorine concentration is high, considerable overheating of a solid material may occur. As far as intermediate titanium oxyfluoride and impurities (in rutile concentrate) may bake, poor mixing of gaseous and solid phases leads to melting of a material and to even bigger deterioration of conditions of phases’ contact. Therefore it is more favorable to conduct a process of TiO_2 formation in a gaseous substance. As particle temperature is almost equal to gas temperature, in these conditions warming of the particle is insignificant [3]. So, the proposed technology allows almost total avoidance of emissions of toxic fluoride-containing matters, assurance of complete fluorination of initial matters, and followed by electrolytic production of titanium powder the process ensures recycle of elemental fluorine as a fluorinating reagent.

In the near future we may expect a breakthrough in the technology of titanium production, which will significantly reduce its production cost; and the cost of titanium will be comparable with the cost of stainless steel. Then, titanium with its excellent corrosion resistance and low density will capture about 10% of the stainless steel market.

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DEVELOPMENT OF TECHNOLOGIES FOR THE EXTRACTION OF RARE EARTH METALS FROM PHOSPHOGYPSUM USING HEAP LEACHING

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Decree of the Government of the Russian Federation № 91–r dated 30 January 2013, approved state program of the Russian Federation "Development of industry and increase its competitiveness" (new edition), program № 15, which is devoted to the development of industry of rare and rare earth metals. In August 22th 2013 was issued a decree № 1339 on the organization and conduct of open tenders for government contracts to perform scientific–research and development works. In the list of those contests was listed R&D work "Development of Industrial Technology for extraction of REM from phosphogypsum". This theme is the basis of our study.

Phosphogypsum – waste processing apatite and phosphorite concentrate on sulfuric acid technology which passes most of the REM contained in concentrates. Average REM content in phosphogypsum is 0.4–0.6%. Phosphogypsum as a source of rare-earth metals is useful due to a number of economically justified reasons: the renewable nature of raw materials (1.7 tons of phosphogypsum per ton of processed apatite) [1], reducing penalties for waste storage because of their processing, building gypsum.

During the processing of the "poor" materials economically viable can be only low-cost technologies. One such technology – is heap leaching, which has recently realized on an industrial scale, both in the Russian Federation and beyond. On the heap leach directed poor gold and oxidized nickel ores, waste physical enrichment of uranium ores, etc.

Despite its attractiveness, heap leaching is limited by the type of material used for lying in a pile. The fact is that the leaching of "heap" is conducted for months and all this time the pile should drain the solution, which irrigates it. Many dispersed materials (which refer to the category of phosphogypsum) are prone to clogging, which leads to disruption of filtration properties of "heap" and as a result – reduce the effectiveness of leaching or its complete cessation.

To overcome this limitation applies granulation material.

The researches of the heap leaching process of phosphogypsum devoted to the determination of optimal conditions for obtaining granular material suitable for heap leaching by the pellet sulfatization method and their impact on access of components and impurities in the solution.

Presently practiced modes producing phosphogypsum pellets having mechanical strength and porosity needed for percolation leaching mode. Also shown the possibility of leaching REM from obtained granules by 93–96% and the degree of extraction of accompanying impurities – phosphorous, fluorine and thorium into solution.

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NEW VARIABLE COMPOSITION PHASES IN THE $2Cu_2S+GeSe_2\leftrightarrow 2Cu_2Se+GeS_2$ RECIPROCAL SYSTEM

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In recent years, copper-germanium chalcogenides have attracted much attention, because these materials have potential applications for using as semiconductors, nonlinear optical materials, superconductors, and as photovoltaic cell materials [1,2].

In order to creation and development of novel preparative methods for controlled synthesis and growth of large single crystals of novel materials it is necessary to investigate the phase relations in the respective systems.

The results of investigation of phase equlibria in the $2Cu_2S+GeSe_2\leftrightarrow 2Cu_2Se+GeS_2$ (A) reciprocal system are presented in this activity.

For experiments, compounds were synthesized from high purity elements in evacuated ($\sim 10^{-2}$ Pa) silica ampoules in the inclined two-zone furnace. The hot-zone was heated up to temperatures ~20–50° above the melting point of the synthesized compounds and the cold-zone to 700 K (sulfides) and 900 K (selenides) somewhat below the boiling point of sulfur and selenium, respectively. The samples of the investigated system (total mass, 0.5 g) were prepared from pre-synthesized and identified starting compounds. Alloys were annealed at 800 K for 1000 h.

Differential thermal analysis (DSC 404 F1 Pegasus Apparatus with S-type thermocouples, NETZSCH) and X-ray powder diffraction (D8 Advance diffractometer using the Cu-K_α radiation) as well as micro-hardness measurement method (MicroMet 5101) were used to analyze the samples.

A number of polythermal sections and isothermal sections at 300 and 800 K were constructed based on experimental results and literature data on boundary quasi-binary systems. It was found that the system (A) is reciprocally reversible and does not have a stable diagonal. The Cu_2GeS_3-Cu_2GeSe_3 section is quasi-binary and characterized by formation a continuous series of solid solutions (γ-phase). The cut Cu_8GeS_6-Cu_8GeSe_6 is non-quasibinary because of the peritectic melting of starting compounds. However, it is stable below the solidus and forms continuous series of solid solutions (δ) between the high-temperature (HT) modification of the starting compounds. The formation of HT δ-solid solutions decreases the temperature of polymorphic transitions of both components. The temperature of polymorphic transition of Cu_8GeS_6 within 0-20mol%Cu_8GeSe_6 decreases from 328K to 310K and for 30 mol% Cu_8GeS_6 this transition is not observed. The polymorphic transition of Cu_8GeSe_6 compound at room temperature is not observed even at 90 mol.%Cu_8GeSe_6. The concentration dependence of the cubic lattice parameters for HT solid solutions follows the Vegard's rule.

The conditions of single crystal growth from non-stoichiometric solution by Bridgman techniques are chosen using the obtained experimental data.

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CHEMICALLY MODIFIED DIATOMIT SORBENTS

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Application of the natural mineral in wastewater is acceptable with environmental and economic view, but generally such materials do not have the acceptable absorption properties. They must be further modified.

Mineralogical and chemical composition of diatomite (Inza deposits in Ulyanovsk region) has been studied for estimation of its possible use. Some technological approaches to obtain sorption materials based on diatomite have been developed.

Original diatomite contains: more than 85% amorphous SiO_2, Al_2O_3 – less than 4%, Fe_2O_3 less than 1,5% , quartz – less than 2%. In order to improve the properties of diatomite, the original diatomite was subjected to various operations: separating solids and sand fraction, thermal and chemical processing, fractionation.

An applying a variety of chemical reagents can alter the chemical composition of natural sorbents for vary their properties (mainly increasing the content of SiO_2 and a molar ratio SiO_2/Al_2O_3). Studies have shown that the ratio of alumina and silica affects on porosity and specific surface of the obtained adsorbents. Such processing of diatomite increases ion sorption. Natural diatomite must be treated to obtain desired properties. In order to obtain high-quality filtering materials thermo-chemical surface treatment is carried out with diatomite alkali metal salts, which promote the formation of poorly soluble silicate compounds of iron. The partial sintering of the points of contact of fine particles to form larger aggregates takes place during heat treatment thereby increasing the filtration rate.

Organic substances can also be used in the modification process to different natural materials. Influence of surfactant changes the microstructure of montmorillonite [1].

For modifying natural sorbent diatomite used agricultural waste – straw. When burning a mixture of straw with crushed porous natural material with a volume ratio of 1:20 there is a double effect - there is modification of the surface of the sorbent products of combustion with simultaneous burning without additional energy costs. The obtained sorbent diatomite can be used for purification of drinking water, galvanic and other impurities from the aqueous solution of heavy metals, hydrocarbons and other compounds [2].

To make granular alumino-silicate sorbents hydrophobic with oil absorption improvers, they were treated with the various organosilicon compounds (alkilsilikon sodium polyethyl-hydroxyl- siloxane etc.) [3].

To increase the degree of extraction of container and oil products used for the treatment of diatomite aluminum salts. A new sorbent was obtained by deposition of the aluminum compounds onto the diatomite surface.

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MODEL OF MOCVD OF NANOSIZED HETEROSTRUCTURES IN HORIZONTAL RACTOR WITH RECTANGULAR SECTION

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There are several basic methods for growing epitaxial layers of solid solutions. MOCVD is the most promising method, as it has a number of advantages: higher performance, lower cost of equipment and the possibility of growth of a wide range of multilayer structures. For example, semiconductor heterostructures based on solid solution InxGa1-xAs/InP, used when producing power electronics devices, microwave electronics, creating lines of fiber-optic communications, gas analyzers and laser radar.

Obviously, for the industrial production of semiconductor structures it is necessary to find optimal growth modes. In addition there is a need to study the effects arising during the growth process as they may affect the parameters of the grown epitaxial layer . Modeling is a promising direction as it allows to solve the that problems. This model includes equations describing heat, energy and mass balance of the reactor. For the numerical studies of complex models used software products based on finite element methods (FEM) and the finite volume metho. Currently widely spread method and FEM software environment that uses this method – COMSOL Multiphysics[1].

We created a 3D model of a real rectangular horizontal reactor MOCVD nanolayers with a rotating substrate holder and induction heating (located at the Research Institute "Polus" named after M.F. Stelmakha). All terms and conditions of the growth process are taken from the real process, and thermal parameters of materials from handbooks. As precursore components used tri- methyl indium (TMIn), tri- ethyl gallium (TEGa) and arsine (AsH3). As the carrier gas is hydrogen (H2). Temperatures are greater than 600 º C and a hundred fold excess of the group V component, the rate-limiting step is the diffusion of III group component. 3D model developed in the software environment COMSOL Multiphysics, includes the Navier – Stokes equations, convection, diffusion, thermal conductivity and electromagnetic potential (based on the equations of the electromagnetic theory Maksvella). After testing of the model [2], we have to expand the set of precursores and reactions for the study of the growth rate of the three – and four-component solid solutions involving Al: AlInAs, AlInGaAs. Layers of such compositions are using to create photodiodes, lasers and other structures with the effect of quantization. Source component for Al is trimethyl-aluminum (TMAl). The numerical studies of the growth rate, temperature and composition, and the coefficients of variation of these parameters coincide with the actual parameters grown nanolayers. Besides the output parameters, examined the effect of the provisions of the inductor of the reactor and the impact on the speed of rotation of layer composition and growth rate. The optimal position of the inductor and the rotation speed was found. The studies showed that in COMSOL Multiphysics software environment possible adequate modeling of MOCVD reactor of horizontal rectangular type with a rotating substrate keeper, while the calculated values of the growth rate and composition of the layers correspond to the experimental values. Then we want to complicate the model by adding a larger number of reactions not only in gas phase but also on the surface.

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SYNTHESIS OF INORGANIC NANOPOWDERS BY ACOUSTOPLASMA DISCHARGE

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In recent years, approaches to synthesis of nanomaterials and nanopowders in particular have been of increasing interest and have attracted a great deal of attention of many groups of researchers. A range of techniques, including sol-gel method, high-energy dispersing, nanoscale biosynthesis have been being applied for several decades already that enabled to obtain nanoparticles of titania, silica, mica, carbon black and other materials.

Nowadays, the problem of low energy consuming techniques for obtaining of nanomaterials becomes increasingly important. In view of ongoing creation of low-waste technologies, the acoustoplasma technique discovered might appear to be advantageous in comparison to traditional methods since it combines the one-step obtaining of nanoparticles and gaseous hydrogen.

Acoustoplasma technique involves the initiating of an electric discharge in a liquid that goes along with ultrasonic power assisted cavitation. In general, the specially designed acoustoplasma reactor involves a reservoir with two immersed electrodes and ultrasonic cavitator. Cavitation bubbles in the liquid phase provide the outstanding characteristics of a discharge and these characteristics have been proven to be governed by the regimes of ultrasonification. Furthermore, ultrasonic power prevents the secondary agglomeration of nanoparticles being synthesized from metal electrodes in electric discharge.

The research has been first aimed toward the acoustoplasma decomposition of hydrocarbons with various molecular weight: it was found that a controlled acoustoplasma discharge in liquid hydrocarbons upon exceeding of the cavitation threshold resulted in carbon nanoparticles exhibiting a peculiar surface morphology and, as further application of these particles is concerned, being highly effective in obtaining of stable nanocarbon dispersions as well as incorporation of these nanoparticles into polymer matrixes. Second, the finding that appropriate ultrasonic treatment in combination with plasma discharge in metalorganic liquids leads to a decomposition of these liquids which in turn allows for a much more effective encapsulation of individual metal nanoparticles with carbon nanolayers that might be effective in view of metal protection, e.g. stainless compounds or particle-binder affinity driven preparation of composite materials.

The second approach involved the acoustoplasma decomposition of elementorganic substances with the purpose of obtaining the solid nanopowders of pure elements such as aluminium, silicium and others as well as nanoparticles of aluminium oxide and silica, respectively. As a result of these experiments, acoustoplasma technique has been demonstrated to be a very effective route to get nanomaterials in two ways in the same reaction – solid powders precipitating in the reaction vessel and gaseous aerosol containing oxide nanoparticles exhibiting the density comparable with that of air. Two perspective avenues of the utilization of these nanopowders have been performed: these nanoparticles could first be deposited on a flat substrate and so created a surface modifying coating and the second option is an entrainment of the nanoparticles into the monomer matrix which can be polymerized afterwards yielding a polymer with immobilized nanoparticles.

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SYNTHESIS OF NOVEL INORGANIC COMPOSITE MATERIALS BY ULTRASONIC TECHNIQUE

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Despite significant advances in the coating technology, there remain many practical limitations in combination of substrate and coating materials to be used. Most of these limitations are caused by the fact that many advanced materials, which could provide new or significantly improved coating performance, differ widely in their properties. For example, it is very difficult to apply a coating of an easily oxidized or/and easily melted metal on the surface of a more refractory metal or ceramic material.

This work presents a new ultrasonic-based dry mechanochemical method for armouring or coating metallic surfaces with other metal or ceramic materials. Two modifications of the method have been examined. In the first one, hard balls and metal or ceramic powder are put into a bowl-shaped resonant chamber which is fixed beneath the surface to be coated. In the second one, only balls are put into the chamber while the surface is previously precoated with a suspension of a liquid and powder. The chamber is set into high frequency vibration by an ultrasonic transducer attached to the chamber bottom. This initiates a chaotic motion and collision of the balls and powder particles, and hammering them into the metallic surface. The results revealed that the method allows the production of various coatings and armoured layers on the metallic surfaces at room temperatures regardless of difference in the properties of materials used.

The method was examined with three substrate/powder material systems: Al/Ti, Al/SiC, stainless steel/Al_2O_3 (substrate/powder) and a number of liquids for precoating. The experiments were performed by using a laboratory-scale equipment. A sample plate of 50×50 mm in size and 2~3 mm in thickness was fixed at the top of the resonance chamber with inner diameter 30 and height of 60 mm. The chamber was set into vibration at a frequency of 21~22 kHz and amplitude of 10~12 μm by using a magnitostrictive transducer powered with a 1kW ultrasonic generator.

The proposed method has no limitation on the area of surfaces that can be processed that makes it usable for many practical applications. Other attractive features of the method are as follows. The coating or armouring process can be performed under room temperature and atmospheric pressure. The method can provide a rapid cold-hardening and nanostructuring of powder particles before coating, as may be necessary. The method can be applied itself or can be combined with other techniques of surface treatment. Besides, the proposed method seems to be attractive for obtaining multi-layer coatings comprising different metal and ceramic particles.

Finally, one more important feature of the ultrasonic method should be mentioned here. Because the interaction time between balls and particles at the sample surface is very short, their deformation or/and embedment into the surface layer occur with very high speeds. This can cause cracking and peeling of thin oxide films, inevitably presented on the surfaces of such easily oxidized metals as Al and Ti, and provide, thus, a better contact between particles and matrix that is of basic importance for the mechanical alloying and coating technology, especially from the standpoint of diffusion bonding or further heat treatment.

This work has been supported by RFBR, projects No. 14-02-31515 and 14-02-00602.

THE INFLUENCE OF MECHANOACTIVATION METHOD ON THE STRUCTURAL AND CHEMICAL CHANGES OF ZEOLITE-CONTAINING ROCKS OF SHIVYRTUY AND HOLINSK DEPOSITS

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One of the fundamental problems of solid state chemistry is the controlled increasing the reactivity of mineral raw materials. Kholinsk and Shivyrtuy zeolite-containing deposits are of industrial importance, not only for the Trans-Baikal region, but for the whole of Russia. In this context, the problem purposeful control of physicochemical properties of natural zeolites with mechanical activation (MA) is extremely important.

In this study, the purpose was a comparative analysis of changes in the structure and chemical composition of the zeolite-containing rocks (DSP) and Holinsk and Shivyrtuy deposits depending on the method MA (manual – in an agate mortar in air at 25°C, 30 min; hardware - in a vibratory attritor dry abrasion, $\nu = 50$ Hz, the mass of milling bodies 0.87 kg, 10 minutes). Chemical analysis of initial and mechanically activated DSP was performed by atomic emission spectroscopy with inductively coupled plasma (Optima 5300DV, PerkinElmer), structure of the samples was studied by infrared spectroscopy (SHIMADZU FTIR – 8400S).

The structure and unique properties of clinoptilolite after MA by any of discussed methods are retained. The results of IR spectroscopy have showed, that displacement of the absorption band of valence vibrations Al (Si)-O_4 in the long wavelength range of 6-8 cm^{-1} DSP Shivyrtuysk deposit indicate a change of the energy parameters of dual rings of the crystal structure of zeolite and are caused by a quantum effect. In addition, as a result of MA and Holinsk, and Shivyrtuy DSP in a vibratory attritor the molecules of CO_2 have penetrated into the structurally disordered mineral matrix and have formed CO_3^{2-} – ions. This is confirmed by the maxima in the IR-spectra at 2385-2340 cm^{-1} (adsorbed CO_2) and 1440–1300 cm^{-1} (ν_s O-C-O).

MA in vibratory attritor DSP Holinsk deposit promotes the appearance of the absorption band at 3695 cm^{-1}, which belongs to the Si-OH groups, localized on structural defects. Moreover, in these conditions, the absorption band of the frame shifts to higher frequencies: initial sample – 594 cm^{-1}, mechanoactivated sample – 600 cm^{-1}. These changes in the IR spectrum are due to the reallocation of exchangeable cations locations – migration of large cavities in small cavities. At the same time, MA in agate mortar practically don't leads to changes in the IR spectrum of this mineral sample. The narrowing of the absorption band at 1045 cm^{-1} and the increasing of the intensity of absorption band at the 453 cm^{-1} only are observed. Thus, MA klinoptilolit-containing rock of Holinsk deposit can efficiently handle in a vibratory attritor than in an agate mortar. The correct selection conditions of mechanoactivation zeolite rocks before using them is an important factor in increasing the activation of cations.

The weight content of SiO_2 and the silica module SiO_2/A_2O_3 of the samples indicated that it belong to mineral species of high silica content: Holinsk (~63% / 7,89–8,11) Shivyrtuy (~67–69% / 9,06–9,69) deposits. Silica module under the influence of MA in the vibratory attritor DSP Holinsk and Shivyrtuy deposits increased by 0.32 and 0.22, respectively, indicating that the increase of surface acid sites. However, this figure as a result of MA in an agate mortar reduced by 0.42 and 0.30 for the studied species.

It can be concluded, that the mechanical activation in an agate mortar or attritor vibration zeolite rocks will be more effective if the mineral rocks impurity are layered aluminosilicate minerals, e.g. smectite or montmorillonite, which, in this case, will pass from the crystalline to the amorphous state. Synergism (joint action) clinoptilolite-smectite in DSP Shivyrtuy deposit allows you to control their structural parameters such as porosity and their catalytic properties.

OPPORTUNITY ELECTROCHEMICAL DEPOSITION OF ALUMINUM - NICKEL ALLOY

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In this paper we investigate the theoretical possibility of intensifying the process of electrochemical synthesis of protective thermal barrier coating aluminum-nickel at room temperature. We propose to use a pulsed deposition method from electrolyte based on aprotic organic solvent containing coordination compounds of aluminum and nickel.

Currently, there is a need to increase the reliability and service life of high-tech products, operating at high temperatures. This poses the problem of the development of fundamentally new materials and methods for their preparation. One solution to this problem is to form the film of heat-resistant coating on the surface of material, e.g. an aluminide of nickel, which provides effective thermal protection material in an oxidizing atmosphere. However, existing methods of obtaining such coatings (self-propagating high-temperature synthesis, hardfacing, spraying, mechanosynthesis, etc.) not only don't give required protection of material, but are complex, energy-intensive and inefficient.

The greatest interest and the relevance acquire electrochemical synthesis methods, which differ low cost and ease of hardware design. These methods of synthesis are possible to produce structures of a given composition and properties by controlling the process parameters. However, the production of aluminum alloys by this method is associated with a number of difficulties. The main difficulties are the inability of aluminum deposition from aqueous solutions and its simultaneous precipitation with other metals due to significant negative standard potential (-1,66 V) [1].

We investigated the possibility of forming an electrochemical alloy of aluminum-nickel, depending on the nature of the solvent. It is necessary to use organic aprotic solvents which do not contain mobile hydrogen atoms, such as ethylbromide, DMF (N,N-dimethylformamide), N,N-dimethylaniline, etc. They are electrochemically stable and may not recovered to potential - 3,0–3,5 V. Their anodic oxidation potential is close to 1,0 .. 1,5 V.

Other factors affecting the electrodeposition process of this alloy are the choice of aluminum and nickel salts and electrolysis mode. It is known the alloy formation in electrochemical systems is only possible when combining of standard potentials. This can be achieved in several ways, one of which is the formation of coordination compounds. Bromide and aluminum chloride with the above solvents to form complexes, which shift the positive standard potential in the region of the side potential of nickel was investigated. Nickelsulphate contrary, forming a complex with these solvents, shifts of nickel deposition potential in the negative region [2]. As a result of combining the potentials of both metals, is possible formation of alloy NiAl, and intermetallic composites of Ni_3Al, Ni_2Al_3.

Electrodeposition mode also plays an important role. When using the DC cathode layer depletion of ions is achieved too quickly. This can lead to changes in the nucleation and complete cessation of the formation of the coating [3]. Pulse mode of deposition provides better control of the microstructure of sediment, allowing adjusting the speed of crystal growth. This leads to more subtle grain structure, stress decrease, high wear resistance. It is also increases corrosion resistance, hardness, porosity, and decreases amounts of impurities. This mode also allows using higher current density, which helps to avoid the limitations of the concentration [4].

We investigated influence of various factors such as the nature of the solvent, the formation of complex ions, electrolysis mode on the process of electrochemical depositing of the protective thermal barrier coating based on aluminum-nickel alloy. Theoretical possibility of this process has been proved.

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ENTHALPY OF MELTING COMPOUNDS Dy_2S_3, Y_2S_3, Lu_2S_3

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Melting temperatures and melting enthalpies for polycrystalline rare earth elements sesquialteral sulfides: γ-Dy_2S_3 (T_{melt} = 1964 K, $\Delta H = 59 \pm 5{,}9$ kJ/mol), δ-Y_2S_3 (T_{melt} = 1880 K, $\Delta H = 34 \pm 3{,}4$ kJ/mol), ε-Lu_2S_3 (T_{melt} = 2030 K, $\Delta H = 55 \pm 5{,}5$ kJ/mol). Reducing the mass of the sample during the heat treatment up to 0,2 % does not change the phase state of the samples, which are homogeneous, after the DSC retained structure type. The calibration graph is built with using standard substances $y = 5x \cdot 10^{-6} + 0{,}003795$. The samples of compounds Ln_2S_3 obtained from oxides Ln_2O_3 in the sulfiding gases H_2S+CS_2 stream at 1320 K. Powders were fused in an H_2S atmosphere in graphite crucibles with using the induction heating. It was conducted physical and chemical analysis of the samples after fusion.

PRODUCTION OF BUTADIENE AND ISOPRENE VIA THE CONVERSION OF LOWER ALCOHOLS

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Butadiene and isoprene are important building blocks for chemical industries; they are majorly produced from petroleum sources. The global demand for butadiene and isoprene is more than 9 million tones, which translates to high demand for their commercially most important polymers some of which are styrene-butadiene rubbers, polybutadiene, styrene-butadiene latex, polyisoprene e.t.c [1, 2].

The rapid development of synthetic rubber industry, depletion of oil reserves due to over dependence on fossil fuels, issues related to the environment and climate changes have adverse effects on the production of these petrochemicals and have necessitated the exploration of other alternative resources and research in this direction.

The combination of ethanol and propyl alcohols with different ratios for the combined production of butadiene and isoprene was studied using lebedeev's reaction as a model. The reaction was carried out in a temperature range of 400 -420^{o}C, flow rates between 1-3 h^{-1} and on a bifunctional contact mass K-64 composed of Mg-Si system, proven to be highly active in the conversion reaction of ethanol into butadiene.

The thermodynamic analysis of this reaction showed high possibility of isoprene production. There is also a possibility of an in situ reaction of isopropyl alcohol with oxygen to simultaneously produce acetone and hydrogen peroxide – considered to be an initiator for the catalytic conversion process of ethanol

Conversion reactions of the mixtures of ethanol, propyl alcohols and oxygen were carried out, in order to study the ratios of the produced butadiene and isoprene.

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SYNTHESIS OF COMPLEXES OF RARE EARTH ELEMENTS WITH BISPHOSPHONATES AND THEIR APPLICATION

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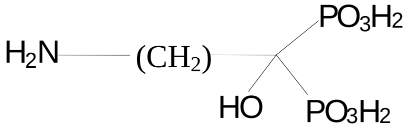
Bisphosphonates are synthetic compounds characterized by a P–C–P group, and are thus analogs of inorganic pyrophosphate. Metal phosphonate chemistry is of great interest for the last years because of potential applications in catalysis, optics, magnetism, exchange and biotechnology.

One area of solid-state chemistry that has shown remarkable growth is the synthesis of porous materials. Porous metal phosphonate materials have increasing interest because of their applications as sorbents, ion exchangers, ionic conductors and catalysts. Among the large number of metal phosphonate compounds many exhibit layered or pillared layered structures. The large variety of organophosphorus acids allows control of the porous structure and chemical properties such as catalytical and adsorption ability, optical behavior [1]. One of the newest applications of bisphosphonates is the cleaning of the waste water from different kind of metals such as cadmium, zinc and lead. In this field there is a great variety of phosphonates which can be used to investigate the relationship of carbon chain to the complexation ability.

In our research work we used the (11-amino-1-hydroxyundecane-1,1-diyl)bisphosphonic acid which also called “lime” and the bisphosphonates with shorter hydrocarbon chain, such as alendronate, pamidronate, neridronate.



First of all we investigate different methods of synthesis such as reaction in solution, autoclave reaction, solid-state synthesis, reflux condensation reaction. The best results give us an autoclave reaction and reflux condensation reaction, but reflux condensation reaction is better due to larger obtained crystals. First, we get crystals of lanthanum-lime, and cerium-lime complexes. The analysis of the structure was done by using AMX400 NMR spectrometer, X-ray powder diffractometer.

After that we use different bisphosphonates, such as alendronate, pamidronate, neridronate. We obtain lanthanum, neodymium and praseodymium complexes, which were analyzed by the same NMR spectrometer and X-ray powder diffractometer. Than we analyze the selectivity and degree of extraction of rare-earth metals from the solution depends on the type of bisphosphonate ligand and rare-earth metal.

Based on the data of their structure we study the possibility of identifying a characteristic dependence of the properties of obtained complexes from the atomic number of the lanthanide. Also by the selectivity data we conclude that bisphosphonates have a promising application in the field of separation of lanthanides.

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PHYSICAL AND CHEMICAL BASES OF SYNTHESIS OF JOINTS ON THE BASIS OF PHASE DIAGRAMMES OF TERNARY RELATIVE SALT SYSTEMS

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From production engineering of reception of joints of members of IIA-group existing now (MF_2, MSO_4, $MMoO_4$, MWO_4 where M - Ca, Sr, Ba), laser crystals applied in the capacity of, luminophores, radiopaque matters, apply a hydrothermal method [1], ceramic production engineering [2], reception of single crystals from melts. Existing production engineering has a number of deficiencies: duration of process with interim homogenization (a ceramic way) or complication in cooking of initial solutes and carrying out of chemical reactions (a hydrothermal way).

The assaying of treble mutual systems on which one ground synthesis of the pointed joints can be carried out is in-process resulted. These systems are included into complex Li, Na, K, M || F, Cl, Br, $ЭO_4$ (Э - S, Cr, Mo, W). In the beginning the pre-award thermodynamic assaying of possibility of realisation of exchange reaction for reference conditions is carried out. In case of exothermic reactions on differential thermal analysis installation registers homogeneous mixture of the reactive salts which are an unstable diagonal of treble mutual systems. Reveal a kickoff of an exothermic reaction which one allows to choose temperature and a time of carrying out of the fusion reaction proceeding with involvement of a fluid phase on massive formation samples.

The prospective production engineering should switch on following basic stages:

1) Preparation of the matters which are unstable products in treble relative system;

2) Weighting, milling and homogenization of a mixture of reactants;

3) Compacting of a mixture of reactants and its delivering in the oven;

4) Annealing at the fusion temperature chosen on the basis of yielded differential thermal analysises;

5) Extraction of a sinter from a reactor, milling and clearing of impurities.

6) Drying and identifying (X-ray analysis method) synthesised compound.

The tendered production engineering of reception considerably reduces temperature and reduces a time of synthesis and as a whole all work cycle. A number of inventions on methods of synthesis of fluorides, molybdates and wolframates of alkaline-earth elements [3] is received.

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THE STRUCTURAL PECULIARITIES AND ELECTRICAL PROPERTIES OF ION-CONDUCTING GLASSES OF $Li_2B_4O_7$-MeF_X(Me - Na, Pb) SYSTEMS

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The development of modern science and engineering demands synthesis of new type of glass like solid electrolytes, that have wide application in microelectronics, in the second class electricity of chemical sources.

For that purpose structural features of glass of $Li_2B_4O_7$-MeFx(Me-Na,Pb) systems are investigated in this work, results of crystallizing directed to infrared spectroscopy, nuclear magnetic resonance, x-Ray and electroconductivity in high temperature area.

In turned out that fluorides in case of containing 20–40 mol% borates of low temperature are considered as crystal phases like $Li_4B_{10}O_{17}$, $Li_2B_8O_{13}$, $Li_2B_4O_7$, in case of larger quantity of fluorides (≥40mol%), $LiBOF_4$, $NaBOF_4$, Pb_2OF_2 oxifluorides and α-PbF_2 are appeared.

It is proved, that lead ion in glass structure occupies two non-similar structural positions, that creates a net forming element $[Pb(O,F)_4]$ and a modifier as well. It is also discovered, that insertion of fluorides and their further multiplication brings to the formation of ending relations of B-F, Me-F, B-O-Me decreasing the degree of glass extended net attachment.

As a result of dilatometric research, it turned out, that in case of large quantity of fluorides (>50mol%) coefficient of thermal expansion of lead glass and glass transition temperature dependence of non-lineal values to composition is explained with the change of extended net forming basic groups. Treat values of coefficient of thermal expansion ($>130\cdot10^{-7}\ {}^0C^{-1}$) of glass containing natrium fluoride are due to high fragmentation of oxifluoride anion net, because of occurence of nonbridging polarized bonds with Na^+ ions in glass structure.

It is also discovered, that in oxifluoride systems, electroconductivity is conditioned by the movement of Li^+ and Na^+ cations and F^- anions. We can neglect participation of H^+ and OH^- groups in the process of electroconduction, because of small quantity of those groups. In case of NaF 40mol% content poly-alkali effect is observed. Unlike NaF containing glasses, lead system glasses have low stability to crystallization. It is contstrued by the extended net forming ability of $Pb(O,F)_4$ oxifluoride and basic glass structural $B(O,F)_4$ groups. In case of glasses containing NaF systems the growth of electroconductivity goes up to the 50mol% content of fluoride, but in case of PbF_2 it is up to 35mol%. It depends on the fact that Pb^{2+} cations, having not large ionic radius, are partially arranged in the cells of glass extended net, meanwhile fluorine-ion is arranged in co-ordination area. The emerged interionic bond with basic net forming element is weak, that is why motion of both inserted anions and cations is high.

A solid electrolyte is worked out, which has got high cation-anion conductivity ($\lg\sigma_{150}=10^{-5}$ $Om^{-1}\cdot cm^{-1}$) and crystallization, with relatively high glass transition temperature (410^0C). It is viscosity is higher than 10^{13} Pa·second in working area of elecrtrolyte.

SYNTHESIS OF RUBIDIUM AND CESIUM PHOSPHATES AND FLUORO PHOSPHATEZIRCONATES (HAFNATES)

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Alkali metal fluorophosphatomerallates (FPMe) represent a new class of chemical compounds with valuable properties. Spontaneous crystallization in the $MeO(NO_3)_2-H_3PO_4-MF(HF)-H_2O$ (Me –Ti, Zr, Hf; M − Na, K, Rb, Cs) systems at room temperature has yielded crystalline and amorphous FPMe with Ti -3 , Zr ~19, with Hf -6. Some of the rubidium and cesium FPMe have displayed a roentgenoluminescence (RL) in the ultraviolet band with an intensity often exceeding that of the known luminophores $BaSO_4$ and CaF_2. The Table presents the compounds having the highest luminous intensity (I).

Synthesis of FPMe and their RL

Compound	Composition of starting solution			I, rel.unit
	MeO_2, wt.%	MeF/Me, m.r.	PO_4^{3-}/Me, m.r.	
$Rb_3H_3Zr_3F_3(PO_4)_5$	2-5	2-4	2	0.45
$CsH_2Zr_2F_2(PO_4)_3{\cdot}2H_2O$ (970°C)*	2	2	1.5	0.43
$CsH_2Hf_2F_2(PO_4)_3{\cdot}2H_2O$(970°C)*	2	2	2	0.68
α-$CsZrF_2PO_4{\cdot}0.5H_2O$ (400°C)**	2	4-5	1.5	0.53
$Cs_2Zr_3OF_6(PO_4)_2{\cdot}3H_2O$(630°C)	5***	4	0.5	0.44
CaF_2 (standard)				0.18

*In brackets: heating temperature, **Isothermal calcinations, *** Starting compound $ZrOCl_2{\cdot}8H_2O$.

Dehydrated FPMe are heat resistant. The $CsH_2Me_2F_2(PO_4)_3{\cdot}2H_2O$ calcined to 970°C forms monophase products $CsMe_2(PO_4)_3$. The hafnium compound $CsHf_2(PO_4)_3$, with its extremely low thermal expansion, actually the least among the known little-expanding ceramics, is an advanced material capable of withstanding all feasible heat shocks [1]. Like $CsZr_2(PO_4)_3$, it may become an active and selective catalyst for alcohol dehydration and a source of cesium-137 for nuclear medicine and radioecology. Earlier it was obtained from a mixture of cesium phosphate and hafnium oxide with B_2O_3 admixed as a flux, or hafnium oxide, phosphoric acid and cesium nitrate or oxalate through a many hour long stepwise heating from 200 to 1200°C.

An original method of $CsMe_2(PO_4)_3$ hydrothermal synthesis has been proposed. Some of the compounds were found to have a high RL intensity in the ultraviolet band.

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SYNTHESIS AND CHARACTERIZATION OF PECTIN-Ag NANOPARTICLES

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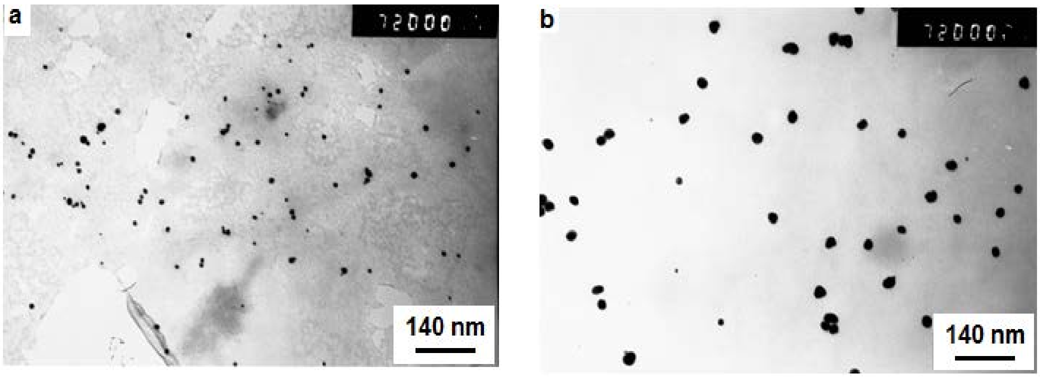
Gold and silver nanoparticles are of interest in medicine and biotechnology due to its potentional applications as catalysts, biomarkers, nanocarriers for local delivery of drugs and etc. Nowadays, there are a lot of synthesis methods of colloidal solutions of nobel metal nanoparticles known [1]. However, the main disadvantage of these techniques is using the toxic reduced reagents. We report here the simple method of silver nanoparticles sols synthesis by chemical reduction of Ag^+ in an alkaline medium using by the natural polysaccharide pectin. This high molecular weight reducing agent (pectin) also acts as a stabilizer of formed nanoparticles.

Silver nanoparticles prepared in the presence of low methoxyl pectin (Pect-LM, the degree of esterification 35–42%) are characterized by a narrow surface plasmon resonance band with a maximum at 400 nm. It is typical for Ag^0 nanoparticles with a diameter about 10 nm. If Ag^+ was reduced by amidated low methoxyl pectin (PectA-LM, degree of esterification 32%, degree of amidation 18%), colloids of Ag^0 nanoparticles with a broad plasmon band with a maximum at $\lambda = 410$ nm have been formed. This sample is more polydisperse and average diameter of silver nanoparticles is about 20 nm. The size of the silver nanoparticles which is estimated by the position of the absorption maximum is in good agreement with the results obtained by transmission electron microscopy (TEM). Calculated from TEM images diameter of the synthesized Ag^0 nanoparticles are 6 ÷ 14 nm if a reducing agent was Pect-LM and 17 ÷ 28 nm for particles in the presence of PectA-LM (figure). The formed pectin-silver nanoparticles are negatively charged, which is probably due to the formation on the Ag^0 surface a negatively charged polysaccharide shell. The zeta potential value of silver nanoparticles synthesized in the presence of Pect-LM and PectA-LM are –36 and – 39 mV, respectively.



TEM-images of silver nanoparticles. Reducing agent: Pect-LM (a) and PectA-LM (b). Duration of reaction – 1 hour, mass ration pectin:silver nitrate = 10:1.

Thus, the developed method allows obtaining aggregativly stable sols of silver nanoparticles with specific characteristics (size, polydispersity and optical properties) at room temperature and without using toxic reagents.

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THE STUDY OF THE PHYSICAL-CHEMICAL INTERACTION OF THE Na_4SnS_4–Tl_2SO_4–H_2O SYSTEM

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In works presents the results of the physical-chemical interaction of the Na_4SnS_4–Tl_2SO_4–H_2O system by chemical and physical-chemical analysis methods (DTA and X-ray diffraction). The interaction have been investigated of different molar ratios of the Na_4SnS_4 and Tl_2SO_4 compounds and it was determined that the molar ratio of the components are different depending on the compounds.

In system Na_4SnS_4–Tl_2SO_4–H_2O have been synthesized of the compounds Na_4SnS_4 by the following scheme for the merger:

$$SnCl_2 \rightarrow SnCl_4 \rightarrow Na_4Sn(OH)_4 \rightarrow Na_4SnS_4$$

Needed for the system 2% Tl_2SO_4solution the prepared by dissolving metal was thallium of dilute of sulfuric acid.

The obtained of the Na_4SnS_4 on the basis on samples prepared (pH=4-9) was added of different molar ratios of Tl_2SO_4 solution. The determined based on the results of DTA and X-ray diffraction of set by the molar ratio of 1:2 of Na_4SnS_4 and Tl_2SO_4 is a combination of Tl_4SnS_4 compounds.

As a result of DTA of this compounds of melting temperature of 736±2 K. The X-ray diffraction results confirmed the identity of this compounds.

In works also of investigated the interaction of Tl_4SnS_4 with SnS_2. It was found that the compounds are Tl_2SnS_3 and $Tl_2Sn_2S_5$ compounds in the Tl_4SnS_4–SnS_2 system.

As a result of DTA the compounds of Tl_2SnS_3 in 698 K melts of konqruent and compounds of $Tl_2Sn_2S_5$ in 733 K melts of inkonqruent.

The relevant units of the standard enthalpy change of formation was calculated of the reactions taking place in accordance with the price of enthalpys:

$$Tl_4SnS_4 + SnS_2 \rightarrow 2Tl_2SnS_3; \qquad \Delta H = -19{,}4\ kC$$

$$Tl_4SnS_4 + 3SnS_2 \rightarrow 2Tl_2Sn_2S_5; \qquad \Delta H = -22{,}8\ kC$$

ALUMINUM OXIDE AND ZIRCONIUM DIOXIDE BY NANO SPRAY DRYER B-90

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Powders of aluminum oxide and zirconium dioxide are widely used for a manufacture process of ceramic, because they have unique properties (high mechanical strength, hardness, wear-resistance, fireproofness, thermal conduction, chemical inertness). Application of nanosize powder instead microsize one allows to improve some properties of ceramic materials.

In this work we propose to use Nano Spray Dryer B-90 for synthesis of aluminum oxide and zirconium dioxide. The innovative piezo crystal driven spray head generates a mist of fine droplets with very narrow size distribution. Nano Spray Dryer B-90 allows collection of fine nanoparticles (separation efficiency >99%) with excellent product yields up to 90 % for small sample quantities <100 mg [1].

The fig.1, a, b shows SEM–images powders receiving from hydroalcoholic solutions of aluminum sulfate and zirconyl chloride. The granules of aluminum oxide have a loose structure but the ones of zirconium oxide have more dense structure. We can see that the powders of Al_2O_3 have a particle size of less than 100 nm and a granule range from 0.5 to 5 μm. The granules of ZrO_2 have more dense structure with range from 1 to 10 μm.

The fig.1, c, d shows SEM – images powders receiving from suspensions. The solution allows receiving a more pure product but productivity is low. The suspension allows receiving a higher productivity but product is not pure [2].

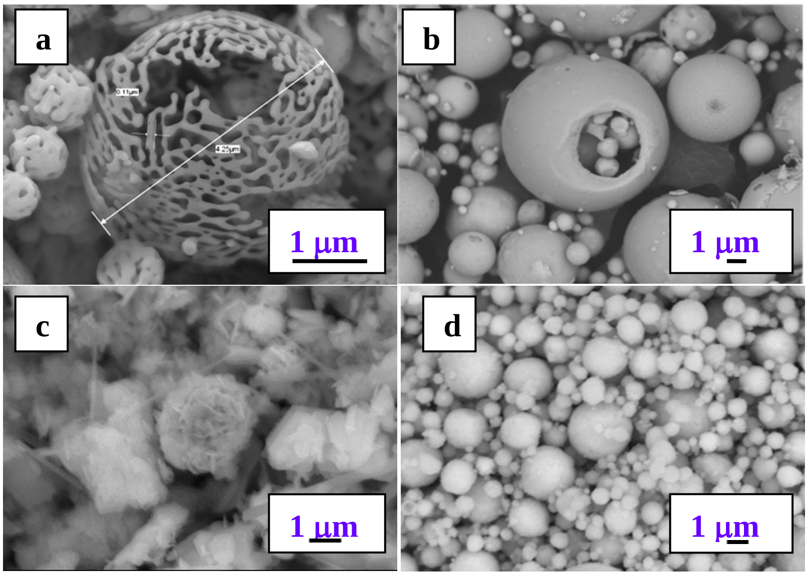

Figure 1. SEM images of powders of alumina and zirconium oxide obtained by spray drying method from solution (a, b) and suspension (c, d).

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SYNTHESIS AND PHYSICO-CHEMICAL STUDY OF SOLID SOLUTIONS BASED ON THERMOELECTRIC Tl_9BiTe_6

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The compound Tl_9BiTe_6 has been the subjects of several studies because presents high thermoelectric figure of merit due to its very small thermal conductivity [1]. Tl_9BiTe_6 is isostructural to Tl_5Te_3 with space group I4/mcm. Thallium lanthanide tellurides, Tl_9LnTe_6, might exhibit good thermoelectric properties like Tl_9BiTe_6 as they are equally isostructural to Tl_5Te_3. Moreover, lanthanide elements are lighter than thallium or bismuth elements resulting in mass fluctuation between the Tl and Ln atoms, which may further lower the thermal conductivity.

In our previous study [2, 3] we published results of investigation of the phase equilibria in Tl-Ln-Bi-Te (Ln-Ce, Nd, Sm, Gd) systems on concentration planes Tl_5Te_3-Tl_9BiTe_6-Tl_9LnTe_6. It was shown that the investigated concentration planes are characterized by formation of continuous field of solid solutions based on Tl_5Te_3 compound.

In this activity the results of investigation of the Tl_5Te_3-Tl_9TbTe_6-Tl_9BiTe_6 (A) system are presented. The samples were prepared by melting of the high purity elements. The required stoichiometric amounts of the individual elements were weighed into silica ampoules and sealed under vacuum. The reactions were carried out in these fused silica tubes by heating in a resistance furnace at 1000 K for 4 hours, followed by slow cooling to 700 K. Finally, the furnace was switched off. The reactions were ground and pressed into pellets and reheated in fused silica tubes at 700 K for a 800h.

Phase equilibriums in the system (A) are investigated by combination of differential thermal analysis (DTA) and X-ray diffraction (XRD) techniques as well as measurements of microhardness and electro-motive force (EMF) at 300-430K temperature interval.

Based on experimental data, a series of polythermal sections and isothermal sections at 700 and 800K of phase diagrams and also a projection of liquidus and solidus surfaces of the system (A) were constructed. Concentration dependences of crystal lattice parameters, microhardness and partial thermodynamic functions of thallium ($\Delta\overline{G}, \Delta\overline{H}, \Delta\overline{S}$) in alloys were determined.

It was established, that system (A) is characterized by formation of continuous field solid solutions with Tl_5Te_3-type structure (δ-phase). However, the system is not quasi-ternary in general due to the incongruent melting of Tl_9TbTe_6 compound.

A series of new quaternary tellurides of system (A) was synthesized, structurally characterized and the thermoelectric properties determined.

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FIXATION OF MAGNETIC NANOPARTICLES ON THE GRAPHENE FLAKES SURFACE

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Nowadays, graphene (G) and its derivatives are being actively studied around the world. One of the topic task is exploration of coordination capabilities of graphene as a ligand to the nanoparticles (NPs). Mutual influence graphene and metal nanoparticles can lead to the obtaining of new materials with unique properties.

The aim of this work was to obtain magnetite and nickel nanoparticles on the surface of graphene flakes.

Synthesis was carried out in several stages. Initially a dispersion of graphene oxide (GO) was prepared using the modified Hummers method [1]. The next step was fixing nanoparticles of metal oxides and metals on the surface of graphene oxide. Finally, the system GO/magnetite and GO/nickel was reduced in supercritical isopropanol in a quartz container in the autoclave.

Variety of structural and spectral methods for characterization of samples was applied: X-ray diffraction analysis (XRD), transmission electron microscopy (TEM); magnetic properties of the obtained nanocomposites were examined too.

From TEM-images of the nanocomposites it is seen that the average size of Ni nanoparticles in the sample GO/Ni was about 7 nm, after the reduction by supercritical isopropanol nanoparticles size up to 40 nm; the average size of Fe_3O_4 in nanocomposite GO/Fe_3O_4 was about 5 nm, and in the nanocomposite G/Fe_3O_4 the particles size increased up to 27,5 nm.

Investigation by X-ray diffraction analysis showed the presence of two different phases for all samples. Nanocomposite Ni/GO contains metal nickel with a cubic lattice structure phases and graphene oxide phase; nanocomposite Ni/G contains metal nickel phase too and graphene phase. The same results were obtain for nanocomposites Fe_3O_4/GO and Fe_3O_4/G, but instead of nickel phase the phase of spinel were observed in these samples.

In magnetic measurement, magnetic hysteresis of nanocomposites was determined and magnetic properties were tested.

Thus, in this paper, a new method for the preparation of magnetic nanoparticles on the surface of graphene by reduction of nanocomposites in supercritical isopropanol was developed.

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INFLUENCE OF THE ELEMENT Nd ON THE PHYSICO-CHEMICAL PROPERTIES OF THE SOLID SOLUTIONS ($Bi_2Sb_5Se_3Te_6I_3$) OF N-TYPE

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It is known that Bi_2Te_3, Sb_2Te_3 and solid solutions based on them are used as materials for the p-branch of thermoelectric coolers. With the introduction of the SbI_3 (Bi_2Te_3. Sb_2Te_3. Sb $_2Se_3$), solid solution of p-type thermoelectric material changes its composition and becomes n-type conductivity.

The disadvantage of these materials is that they are layered and easily crushed. In order to increase the strength of a solid solution ($Bi_2Sb_5Se_3Te_6I_3$) n-type the elementary Tb Nd up to 20 mol.%. was added.

PHYSICAL AND CHEMICAL PROPERTIES OF $La_{1-x}Ca_xCoO_3$ PEROVSKITES PREPARED VIA MECHANOCHEMICAL ROUTE

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Due to high mixed ionic (O^{-2}) and electronic conductivity at elevated temperatures Ca substituted $LaCoO_3$ perovskites have technological interests as materials for oxygen permeable membrane, electrodes in solid oxide fuel cell, oxidation catalysts or oxygen sensors. Preparation route may play a very important role in their properties. Mechanochemical route is a new power efficient and waste less method for preparation of mixed oxides.

The goal of the paper is preparation of $La_{1-x}Ca_xCoO_3$ perovskites via mechanochemical (MC) route and investigation of their properties.

$La_{1-x}Ca_xCoO_3$ (x=0, 0.1, 0.2, 0.3, 0.4, 0.4, 0.6, 0.7, 0.8, 0.9, 1) perovskites were prepared from La_2O_3, Co_3O_4 and CaO oxides taken in needed proportions. After their MC treatment in the APF-5 planetary ball mills during 3 min, powders were air calcined at 1100 C for 5 hours. The ratio of the weights of milling balls and oxides powder was equal to 10:1, acceleration achieved in the drums of the mill ~ 40 g.

XRD patterns were obtained in the range 10–80^o with a X'TRA diffractometer. TEM data were obtained with JEM-2010 instrument. Specific surface area was determined by Ar desorption at 300^{o}C. Catalytic activity in methane oxidation was studied with 0.25–0.5 mm particles in flow reactor in the range of 350–600^{o}C. Samples weight and volume were 1 g and 0.6 cm^3, correspondingly. Reaction mixture (0.5% CH_4 + 9% O_2 in He) flow was 2.4 l/h. TPR experiments were carried out for particles of 0.25–0.5 mm. Samples (50 mg) were pretreated in oxygen at 500^{o}C and after cooling in oxygen heated up to 900^{o}C in hydrogen (10% H_2 in Ar, gas flow 40 cm^3/g) with velocity of 10 ^{o}/min.

According to X-ray data all as prepared samples in addition to perovskite structured oxides contain admixtures of Co_3O_4 and/or CoO phases. Increase in Ca content leads to change perovskite structural modification from hexagonal (x<0.4) to cubic (x>0.4). At that samples with x = 0.4–0.7 may contain both perovskite structural modifications. Starting from x = 0.6 admixture of $Ca_2Co_2O_5$ with brounmillerite structure is appeared while perovskites content is decreased. Samples with x=1 consists of $Ca_2Co_2O_5$, Co_3O_4 and $CaCO_3$.

According to TEM data perovskite particles consist of the blocks, their size is varied from 100 nm up to 1 mkm, while Co_3O_4/CoO particles are of 10–50 nm and aggregated. Perovskites with rhombohedral modification are formed only up to x=0.2. Cubic perovskite is $La_{.6}Ca_{0.4}CoO_3$. In addition calcium and/or lanthanum oxides were detected in the samples. Data obtained by TEM revealed formation of 3 main phases in the system – $La_{1-x}Ca_xCoO_3$ (x = 0–0.2), $La_{.6}Ca_{0.4}CoO_3$ and $Ca_2Co_2O_5$. All other samples are a mixture of the main phases and initial oxides as a rest. Hence unlike the ceramic route phases $La_{.6}Ca_{0.4}CoO_3$ and $Ca_2Co_2O_5$ may be prepared via MC route in the $La_{1-x}Ca_xCoO_3$ system.

According to TPR data Ca adding leads to increase total hydrogen consumption as well as consumption up to 500^{o}C that may be due to Co^{+4} formation as a result of substitution in perovskites. Its quantity is lower than theoretical (x).

Samples catalytic activity in methane oxidation depends on the samples composition and testing temperature. Increase the testing temperature leads to increase, while Ca adding leads to decrease the activity very probably due to its surface segregation because no correlations between the activity and total as well as up to 500^{o}C hydrogen consumptions were revealed. At that there is a low wide maximum activity for samples with x = 0.3–0.5 that may be due to formation of interphase boundaries and surface lower bond oxygen form, consequently, by analogy with earlier studied $La_{1-x}Ca_xMnO_3$ system.

MICROSTRUCTURE OF $Li_{3x}La_{2/3-x}TiO_3$ CERAMICS SYNTHESIZED FROM SOL-GEL PRECURSORS

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Solid solutions on a basis of the lithium-lanthanum titanate $Li_{3x}La_{2/3-x}TiO_3$ ($0.21 \leq 3x \leq 0.50$) are stable in air and represent a promising material for solid electrolyte due to their ionic conductivity of the order of 10^{-3} S/cm. At present the $Li_{3x}La_{2/3-x}TiO_3$ (LLT) solid solutions are perspective as separators of the low and medium-temperature lithium current sources and as membranes in Li-air batteries [1].

In this study the LLT powders with x=0.11 was prepared by sol-gel method using citrate-nitrate precursors. As synthesized the LLT powders were characterized using X-ray powder diffraction, DSC/TG, SEM, and impedance spectroscopy. Conductivity measurements were carried out in the frequency range of $10\text{-}2 \cdot 10^6$ Hz at a constant voltage of 0.1 V with the help of a Z-2000 impedance meter. It was determined that after sintering of the synthesized powders at 1000°C for 2 h the single-phase well crystallized tetragonal $Li_{0.33}La_{0.56}TiO_3$ (JCPDS card 87-0935) was formed. As a result of the powders microstructure studying by SEM it was established that grains of $Li_{0.33}La_{0.56}TiO_3$ ceramics had a habitus with rectangular section (Fig.) what corresponds with the XRD-data about tetragonal symmetry of a crystal lattice. According to IR-spectroscopy the synthesized $Li_{0.33}La_{0.56}TiO_3$ samples have perovskite structure with characteristic absorption band in the areas 580–600 and 750–780cm^{-1} what corresponds valence vibrations of Ti-O bond in TiO_6 octahedrons [2].

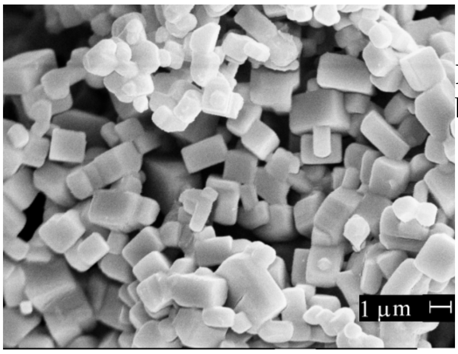

Fig. SEM image of the LLT powder prepared by sol-gel method after sintering at 1000°C.

The specific surface of the LLT powders was 0.8 m^2/g after precursor sintering for 2 h at 1000°C (the average LLT particle size was 1.5 µm). Analysis of the size distribution of $Li_{0.33}La_{0.56}TiO_3$ powders after precursor sintering for 2 h at 1000°C showed that the system was polydisperse (the particle size changes in the range of 1 – 15 µm). The system of crystallographic (101) and (110) planes with Bragg angles of $2\theta = 25.8°$ and $2\theta = 32.7°$, accordingly, was chosen for calculation of the coherent scattering regions (CSRs). The CSRs size was determined according to the Selyakov-Scherrer formula. Analysis of broadening of diffraction maximums indicates that the size of primary LLT crystallites after sintering at 1000°C was 94 nm according to the (101) plane and 98 nm according to the (110) plane. Thus, the sol-gel synthesis provides lithium-lanthanum titanate $Li_{0.33}La_{0.56}TiO_3$ powders with particles of submicron size and bulk conductivity of $(8\text{-}9) \cdot 10^{-4}$ S/cm at the room temperature.

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COMPOSITES CONTAINING NANOSIZED TITANIUM AND FERROUS OXIDE AND OXYFLUORIDE SYTHESIZED IN PLASMA OF HIGH-VOLTAGE DISCHAGE

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Nanocomposites containing nanocrystalline titanium oxide and oxyfluoride as well as fluorocarbon and carbon components have been synthesized by method employing a combined destruction of titanium electrodes and fluoroplast in the plasma of pulse high-voltage discharge under air and argon atmosphere conditions. Variations of the experimental conditions allowed controlling nanoparticles sizes (from 1 up to 200 nm) and morphology (Fig. 1). The samples annealing at 800°C resulted in transformation of the composite material into nanodispersed rutile. The possibility of application of the obtained composites as anode materials in lithium batteries has been demonstrated: the capacity attained on the test sample was equal to 1185 mA∗h/g.

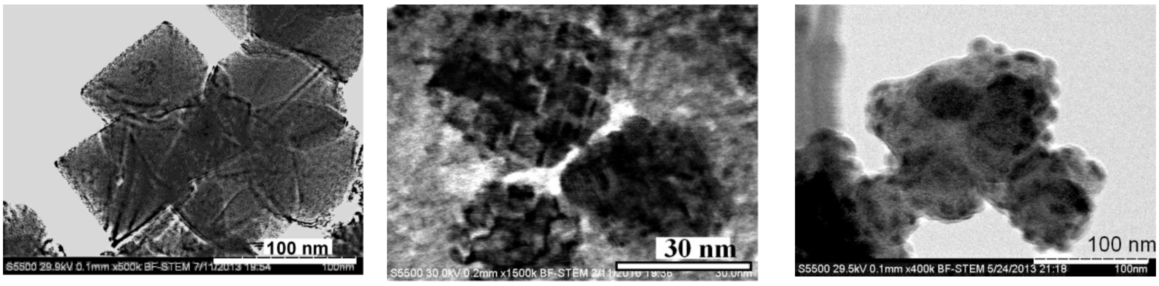

Fig. 1. ESM morphology different samples.

Nanocomposites containing nanocrystalline ferrous oxide and oxyfluoride and doped different elements (Ni, Cr, Mn, Al, Si) have been synthesized by method employing a combined destruction of various ferrous containing alloy electrodes and fluoroplast in the plasma of pulse high-voltage discharge under air. Various hard magnetic materials characterizing different asymmetry of magnetic hysteresis loop (max asymmetry -1160 O.e. +460 O.e.) and containing superparamagnetic particles was obtained. The samples annealing at 800°C resulted in transformation of the composite material into different elements doped hematite. It find out that into high temperature phase Morin transition is absent for hematite containing Cr, Al impurities.

Polycrystalline ferrous oxide have been synthesized by method destruction of ferrous containing alloy electrodes in the plasma of pulse high-voltage discharge under air. Soft magnetic materials was obtained.

Obtained results is demonstrated that using method is perspective for synthesis of various functional materials.

SYNTHESIS OF ZEOLITES OF THOMSONITE TYPE

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Thomson refers to zeolites , which found practical application. It has found application in medicine and food industries. It is used as food additives, which are excreted harmful metabolites without affecting the proteins and other macromolecules. Harmful substances received from food and excreted from the body [1].

We were the first synthesized zeolite of thomsonite in the halloysite (H) - dolomite (D) of systems. Experiments on hydrothermal synthesis of zeolite of thomsonite scheduled conducted in autoclaves like “Mory” with a volume of 20 sm^3 at 180°C, the filling factor F = 0.8 autoclave for 2 days. The concentration of the thermal solution was NaOH 1.5 N, the ratio of the initial components H: D = 1:1.

Phase and chemical composition of the initial and final products was determined by X-ray diffraction (DRON-3.5; CuK_α-radiation, Ni-filter), thermography (derivatograph Q-1500D) and X-ray spectral (SRM-18) methods of analysis.

X-ray diffraction and X-ray spectral analysis techniques found that as a result of the hydrothermal synthesis of the product is a type of zeolite of thomsonite. This zeolite is crystallized in the orthorhombic system with unit cell parameters a = 13.07 Å, b = 13.08 Å, c = 13.18 Å [2].

Thermographic analysis method established area of dehydration, water content and temperature stability of thomsonite. Zeolitic character of the resulting sample is determined by calculation of oxygen volume (V_0), the study of de-and rehydration and cation exchange capacity. As it is known, the total water content at zeolite framework is determined by the volume of voids accessible to water molecules. It is therefore of interest to calculate the amount of oxygen V_0 (the volume of one molecule of oxygen in Å) [3]:

$$V_0 = V_m/2p + q,$$

where V_m – absolute molecular volume, 2p – by oxygen molecules in the aluminosilicate framework, q – by molecular oxygen in the water located in the cavities of the frame.

Graphic dependence of molecular volume V_m on the number of oxygen atoms (2p + q) is linear for the zeolites, for which V_0 is approximately 21.66 Å. We calculated the value of the oxygen V_0 amount in is 21.60 Å.

This work was supported by the Science Development Fund under the President of Azerbaijan Republic – Grant No. EİF/GAM-1-2011-2(4) -26/20/4.

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PECULIARITIES OF TITANIUM SURFASE MODIFICATION IN ORGANIC AQUEOUS ELECTROLYTES WITH VARIOUS CONDUCTIVE ADDITIVES

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We investigated the electrochemical oxidation of titanium in water-containing organic electrolytes at potentials of 2–14V in the presence of 0.05–0.75% various conductive additives affecting the product of electrochemical modification. The formation of titanium dioxide occurs at a concentration of more than 0.25% NH_4F. The formation of titanium nitride occurs at a concentration of less than 0.25% NH_4F, or at a concentration of less than 0.5% KF, $LiClO_4$, KOH, NH_4SCN.

We demonstrated and substantiated the possibility of formation of titanium nitride by anodic polarization of titanium surface and presented results of research of properties of titanium nitride films.

Conductive films from light yellow to bronze color are formed during the electrochemical processing of titanium layers in before-mentioned electrolytes. A result of diffraction analysis shows the correspondence of obtained films to the titanium nitride.

We have identified: the full chemical resistance of the films to the concentrated and dilute hydrochloric, nitric and sulfuric acids, cold concentrated and dilute hydrofluoric acid and to a cold solution of potassium hydroxide; the thermal stability of the samples by heating up to 500°C (at higher temperatures the studies were not conducted). According to the elemental analysis data the composition is described by $TiN_{0,\ 88}$ – $TiN_{1.18}$ what means that mononitride titanium forms during the anode polarization. The resistivity of the layers was less than 2 Ohm·cm.

The process of formation of titanium nitride films in electrolytes with conductive additive NH_4F describes the general equation:

$Ti + NH_4^+ \rightarrow TiN + 4H^+ + 3e^-$, ($\Delta G = -214{,}9\ kJ\cdot mol^{-1}$),

and consists of the following stages:

1. oxidation of the ammonium cations at the anode

$2NH_4^+ \rightarrow N_2 + 8H^+ + 6e^-$;

2. anodic process of dissociation of molecular nitrogen

$N_2 \rightarrow N_{(ат)}$;

3. the interaction of atomic nitrogen with titanium and formation of titanium nitride variable composition with the general formula Ti_xN_y

$xTi + yN_{(ат)} \rightarrow Ti_xN_y$.

In electrolytes with background additives that do not contain the element N, a source of atomic nitrogen is dissolved in the electrolyte molecular nitrogen. In this case, the mechanism of the process involves only the second and third stages.

We have established that stable processes of titanium nitride formation are observed at potentials of 2–14V in a water-containing ethylene glycol in the presence of 0,05–0,25% NH_4F or of less than 0.5% KF, $LiClO_4$, KOH, NH_4SCN. Obtained samples correspond to titanium mononitrides.

SYNTHESIS OF COMPOUND $BaPr_2MnS_5$

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According to [1, 2] in the system BaS – Pr_2S_3 – MnS is formed the compound $BaPr_2MnS_5$, tetragonal structure, space group I4/mcm. Temperatures, character of melting and concentration interval of existence $BaPr_2MnS_5$ are not known. The phase equilibria in the BaS – Pr_2S_3 – MnS are not studied. By X-ray and microstructural analysis studied a sample containing 33.3 (3) mol. % BaS, 33.3 (3) mol. % Pr_2S_3, 33.3 (3) mol. % MnS, prepared at different temperatures . On the diffraction pattern of the sample crystallized from the melt , there are reflections starting sulphides of MnS and γ-Pr_2S_3. The sample contains 2 phases according to analysis of the microstructure. $BaPr_2MnS_5$ phase reflections on the diffraction pattern are not found. Lack of reflections $BaPr_2MnS_5$ points on the instability phase at high temperatures. The phase will melt incongruently or decompose on the solid state reaction. At the annealing of the sample at a temperature of 1500-1550 K was a partial $BaPr_2MnS_5$ phase formation at surface of the crystal γ-Pr_2S_3. The microstructural analysis showed that most of the sample occupy crystals γ-Pr_2S_3, found traces of the eutectic mixture. At sintering the initial mixture of sulfides BaS Pr_2S_3, MnS in ratio 1:1:1 at 1170 K for 500 hours obtained sintered powder. According to X-ray analysis, on diffraction pattern are present reflections characteristic for $BaPr_2MnS_5$ phase. Reflections of cubic structures MnS and γ-Pr_2S_3, orthorhombic structure α-Pr_2S_3 are not found. Part of the powder particles which are most closely in contact with each other are sintered, which indicates a low melting point of this compound.

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SORPTION RECOVERY OF SCANDIUM FROM THE SULFURIC ACID SOLUTION ON A GRANULAR TITANIUM PHOSPHATE

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Waste and circulating industrial solutions of a number of industries (hydroxo zirconium sulfate, uranium oxide , pigmental titanium dioxide , etc.) contain scandium and other rare earth elements in small amounts (from several to several tens of mg / l) due macro amounts of iron, aluminum, calcium, magnesium, and other salts. It is expedient to use ion exchange (or sorption) method for efficient recovery of valuable components.

The sorption recovery of scandium from sulfuric acid solution has been researched from (g / l): Sc 0,01, Y 0,01, K 1,0, Mg 0,4, Ca 0,4, Fe (III) 0,3, Al 0.7 on the samples of spherically granulated titanium phosphate synthesized in the Institute of Sorption and Problems Endoecology NAS of Ukraine [1]. According to XRF, titanium phosphate is amorphous, according to the study of low-temperature nitrogen adsorption, the pore volume of the sorbent is 290 ml / g. Sorbent was used with a size of particles 0,5 ÷ 1 mm.

We have found that the distribution ratio of Sc increases with increment of molar ratio P: Ti and is maximum for P: Ti = 1,8. According to the kinetic experiment, the equilibrium time is 2 hours.

It has been shown that decrease in pH of the solution from 5 to 1.7 leads to decrease in sorption degree of Sc by 11.1%, at the same time increase of acidity leads to decrease stability of titanium phosphate. In the process of neutralization of the sulfuric acid solution with forming of iron hydroxide (III) precipitate noticeable sedimentation of scandium begins when pH is 3.2 and more.

We have studied desorption of scandium from the saturated titanium phosphate in dynamic conditions. The degree of desorption of scandium by nitric acid solutions increases with its concentration, but even for 8M HNO_3 it does not exceed 63.3%.

These data indicate that the use of titanium phosphate for scandium extraction from sulfate solutions with complex composition is expedient if pH is more than 3.2, in this condition the coprecipitation of scandium is insignificantly, scandium capacity of sorbent is maximum and sorbent stability is acceptable.

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SYNTHESIS OF MIXED FORMS Zn-Ca OXIDES FINE POWDERS IN CHLORIDE MELTS

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Fine dispersed zinc and calcium oxides can be applied in electronic and pharmaceutical industry, as well as in production of adsorbents, catalysts, sensors, abrasives, and ceramics with excellent operating characteristics.

It was shown, that while feeding of air or oxygen to molten chlorides of magnesium, calcium or zinc reaction of chloride-ion oxidation occurred resulting in formation of corresponding nanosized (ZnO) as well as coarse-crystalline, but nanostructured (MgO) metal oxide and gaseous chlorine [1].

Powders of mixed calcium and zinc oxides were synthesized by reaction of molten zinc and calcium chlorides by bubbling air or oxygen (2,5 l/hr) at 600^{o}C, and different molar ratio of the initial chlorides (mixed in Ca:Zn 1:1, 1:2 molar ratio). Metal oxides generated in such way were retrieved through dissolving of reaction mixture in ethanol by long heating followed by centrifugation. Oxides powders were then dried at 100–130°C and calcined at 650°C for five hours.

It was established that the chlorine yield depend on the molar ratio of chloride in the mixture. The chlorine and oxide formation rate obeys a zeroth-order rate equation. Mixed zinc and calcium, formed during oxidation reaction were analyzed with the help of optical and atomic force microscopy, and XRD-analysis. Dispersity, chemical composition and surface area for some samples were defined. XRD analysis data indicated that CaO and ZnO were the only reaction products.

It was established with the help of atomic-force microscopy that Ca and Zn oxides grain size in their mixture was about 100–200 nm (See fig.).

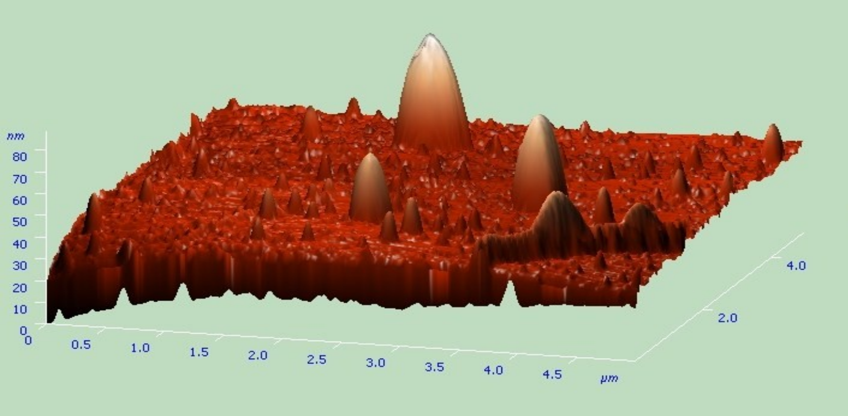

Fig. Image of ZnO–CaO particles on graphite substrate.

Data acquired allow saying that reaction of molten chloride oxidation is of interest to produce metal oxides. It is possible to synthesize with help of this method fine dispersed zinc and calcium oxides of high purity.

This work has been performed with financial support of RFBR, project No. 13-03-00166_a.

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SYNTHESIZING A NEW COMPLEX SULFIDE $SrHoCuS_3$

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For the first time ever complex sulfide $SrHoCuS_3$ has been synthesized and its crystal structure has been defined by using X-ray powder diffraction (figure, table).

Sulfide SrS has been synthesized through reduction of $SrSO_4$ in current of H_2 at 1070 K for 15–20 hours, compound Ho_2S_3 has been synthesized from oxide in current of H_2S and CS_2 at 1300 K, that is indirect method; Cu_2S – from elemental Cu and S through the method of vacuum sealed quartz ampoules. According to X-ray powder diffraction, the simple sulfides were single phase. Within the error of chemical analysis, the sulfides had the stoichiometric compositions. Compound $SrHoCuS_3$ has been synthesized by alloying original sulfides in the ratio $2SrS:1Ce_2S_3:1Cu_2S$ in alundum protected graphite open cup in open quartz reactor. Reactor has been vacuumed and blown with argon. Cup had been heated in the high frequency generator, than it has been held for 2 min. close to pouring point whilst being constantly shaked. The moment of pouring has been observed. Heating has been repeated three times. There wasn't interreaction between compounds and cup materials. Sample had been alloying for 2 months in vacuum sealed quartz ampoule at 1170 K.

X-ray pattern was made within the range $12^\circ \leq 2\theta \leq 157^\circ$ by using diffractometer PANalytical X'Pert PRO (CoKα radiation, Fe filter, PIXcel detector). Cell parameters were determined with the ITO software. The crystal structures were refined by the derivative difference minimization (DDM) method in the anisotropic approximation for all atoms with consideration for the effects of preferred orientation, anisotropic broadening of peaks, and sample surface roughness and displacement. The reliability factors $R_{DDM} = 4.29\%$, $R_F = 1.91\ \%$.

Compound $SrHoCuS_3$ is orthorhombic system, space group of symmetry is Pnma, structural type is Eu_2CuS_3 with elementary cell parameters are: a = 10.1487(1), b = 3.9332(1), c = 12.9524(2) Å (figure). Structure of compound $SrHoCuS_3$ can be described with 2-D layers ($CuHoS_3$), compounded CuS_4-distorted tetrahedrons and HoS_6-distorted octahedrons, in a-b plane. There are Sr ions between these layers.

Atomic coordinates and equivalent thermal parameters in the structure of $SrHoCuS_3$

Atom	x	y	z	U_{eq} Å^2
Ho	0.01000(14)	1/4	0.74458(14)	0.012(3)
Sr	0.76421(33)	1/4	0.00197(10)	0.016(3)
Cu	0.24059(32)	1/4	0.22142(14)	0.018(3)
S1	0.0551(7)	1/4	0.1167(5)	0.014(3)
S2	0.4201(7)	1/4	0.10887(45)	0.010(3)
S3	0.2577(7)	1/4	0.82631(24)	0.012(3)

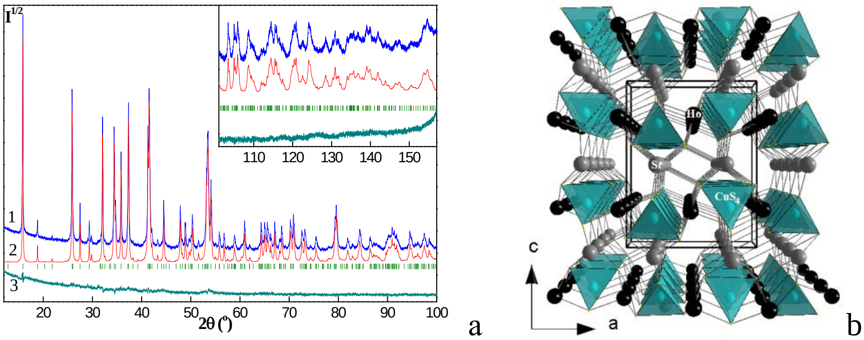

Fig. Experimental, (2) calculated, and (3) difference X-ray diffraction patterns of $SrHoCuS_3$ after DDM refinement (a). Geometrical projections [010] of the structure of $SrHoCuS_3$ (b).

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SYNTHESIS AND CRYSTAL STRUCTURE OF COMPOUND $EuDyAgS_3$

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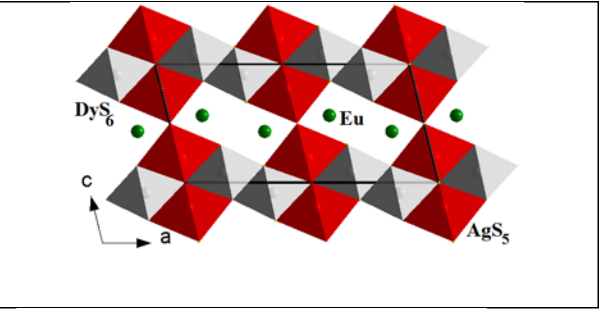
Synthesis of $EuDyAgS_3$ compound has been carried out in two ways.

First way was alloying original sulfides in ratio $2EuS{:}1Dy_2S_3{:}1Ag_{2-x}S$. EuS, Dy_2S_3 sulfides have been synthesized from oxide in a flow of a mixture of gaseous H_2S and CS_2 at 1300 K, that is indirect method. $Ag_{1.985}S$-compound has been synthesized from elemental Cu and S through method of vacuum sealed quartz ampoules (stoichiometry of Ag_2S isn’t accurately synthesized; composition of sulfide phase is $Ag_{1.99\text{-}1.97}S$). Sulfides placed in graphite open cup has been placed in quartz reactor that had been vacuumed and than has been blown with argon. Cup had been heated by inductive effect in the high frequency generate (HFG), then it has been held for 2 min. close to pouring point whilst being constantly shaked. The moment of pouring has been observed. Heating has been repeated three times. Sample had been alloying for 3 months in vacuum sealed quartz ampoule at 1170 K. Based on X-ray powder diffraction in samples there is $(Eu,Dy)_3S_4$ dirt (16%) besides $EuDyAgS_3$ main phase (84%) is isostructural $BaErAgS_3$. Second way is alloying EuS, Dy_2S_3, Ag and S in ratio $2EuS{:}1Dy_2S_3{:}1Ag_2S$ in graphite open cup placed in vacuum sealed quartz ampoule. Ampoule had been heated to 1570 K in electrical furnace and than it has been held for 30 minute. Cooling was run in furnace turned off. Ampul contain sintered sample had been placed in open quartz reactor, that had been vacuumed and than has been blown with argon. Cup had been heated by the HFG, than it has been held for 10 min. about pouring point. Cubic system compound $EuDyAgS_3$ has been synthesized through this way. Space group of symmetry is Fm3m, structure type (ST) is like $AgBiS_2$ with elementary cell (e.c.) parameters are: a = 5.697 Å (figure 1a). After compound $EuDyAgS_3$ has been staved at 1170 K, it has monoclinic system, space group of symmetry is C12/m1, ST like $BaErAgS_3$ with e.c. parameters are: a = 17.2052(19), b = 3.9448(4), c = 8.2979(7) Å (figure 1b, table). There is block-laminated organization in Crystal structure of compound $EuDyAgS_3$. There are 3-D structure formed of DyS_6 octahedrons and AgS_5 trigonal bipiramids that include Eu ions in channels. There are 2-D layers made of one-capped EuS_7 trigonal prism in b-a .

Atomic coordinates and equivalent thermal parameters in the structure of $EuDyAgS_3$

Atom	x/a	y/b	z/c	U, Å^2	
Dy	0.1635(4)	0	0.0840(19)	0.0164(32)	
Eu	0.1345(3)	0	0.5664(20)	0.0046(28)	
Ag	0.5114(8)	0	0.2073(8)	0.063(5)	
S1	0.3272(14)	0	0.145(7)	0.003(15)	
S2	0.6777(15)	0	0.309(7)	0.016(18)	
S3	0	1/2	1/2	0.011(10)	
S4	0	0	0	0.013(13)	

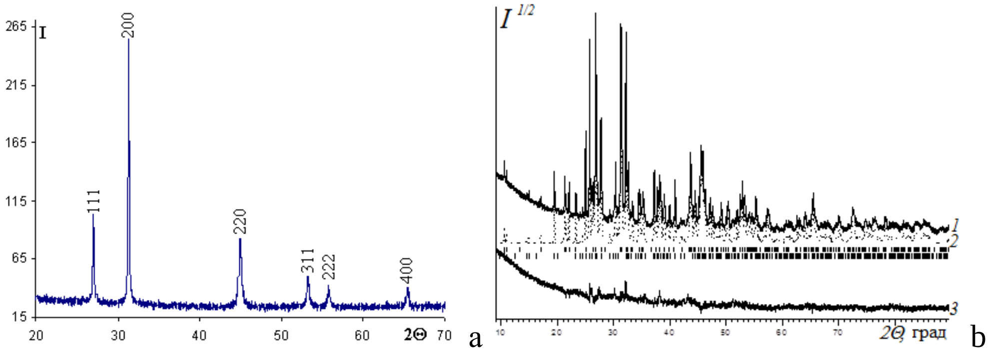


Fig. (1) Experimental, (2) calculated, and (3) difference X-ray diffraction patterns of $EuDyAgS_3$ after DDM refinement.

This work was supported by SDW № 2014/228 № 996.

PREPARING OF FLUORESCENT MATERIALS BASED ON ALUMINATES OF ALKALINE EARTH ELEMENTS

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Alkaline earth aluminate activated by rare-earth ions (RE^{n+}) possesses intensive luminescence upon UV excitation. Compared with traditional sulfides, such phosphors have the advantages of perfect luminescent efficiency, long persistence time, good stability and no radioactivity pollution, so they have been studied extensively and are widely used in luminescent porcelain, the guidepost of speedway, airfields, buildings and so on [1].

The solid-state reaction process has been used intensively for phosphor synthesis, but this process often results in poor homogeneity and requires high calcinating temperature. With the development of scientific technologies on materials, several chemical synthesis techniques, such as coprecipitation, sol–gel, microwave, Pechini and combustion synthesis methods have been applied to prepare rare earth ions activation alkaline earth aluminate and its phosphors. All of these methods were conducted in liquid phases so that each component can be accurately controlled and uniformly mixed [2].

In this paper, a sol-gel process was chosen to prepare RE^{n+} doped MAl_2O_4 (M = Ca, Sr, Ba) luminescence phosphor.

The mixtures of components to produce a complex oxide ($M_{0,985}Eu_{0,015}Al_2O_4$, $M_{0,985}Tb_{0,015}Al_2O_4$, $M_{0,955}Eu_{0,015}Dy_{0,03}Al_2O_4$, $M_{0,955}Eu_{0,015}Tb_{0,03}Al_2O_4$, $M_{0,955}Eu_{0,015}Nd_{0,03}Al_2O_4$) were prepared from aqueous solutions of aluminum nitrate nonahydrate (Al^{3+}), alkaline earth metal nitrate (M^{2+}) and citric acid monohydrate (H_4Cit). Oxides of RE^{n+} were dissolved at the nitric acid. The starting components containing calcium and aluminum cations were taken at a stoichiometric ratio; the molar ratio between citric acid (H_4Cit) to the total amount of the cations ($Ca^{2+} + Al^{3+} + RE^{n+}$) was 3 : 1 [3].

The final composition of the products was estimated using Rigaku MiniFlex 600 X-ray diffractometer (CuKα radiation). The measurements were carried out at room temperature between 3 and 80 degrees. The surface morphology of the end compound was investigated by scanning electron microscopy (SEM) on a Hitachi TM 3000 instrument. Photoluminescent (PL) analyses including excitation spectra, emission spectra were conducted on a CM 2203 spectrofluorimeter with Xe lamp at room temperature. The UV-excitation from a xenon lamp was centered at 240 nm.

The excitation and emission spectra of phosphors obtained using sol-gel technology, which are almost the same in shape except for their intensity. The excitation spectra show a broad band ranging from 210 to 350 nm with maximum at 240–300 nm. Luminescence spectra indicate that the europium ion in the alkaline earth aluminate is in the oxidation state +3. Maximum emission corresponds to the red part of the spectrum. The luminescence spectrum MAl_2O_4: Tb^{3+} there is a strong line corresponding to the green part of the spectrum.

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THE EFFECT OF INTRAMOLECULAR HYDROGEN BOND IN ITACONIC ACID ON FORMATION OF COBALT ITACONATE

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The formation of intra-molecular hydrogen bond (IMHB) in molecules of dicarboxylic acid has a considerable effect of formation of metal carboxylates. For maleic acid (MA) formation of IMHB is typical, which leads to considerable discrepancy of dissociation constants. Thus MA can donate only one carboxylic group for displacement, behaving as a monodentate ligand and forming mostly acidic salts. Formation of acidic or neutral metal carboxylates then affects the structure of carboxylates in condensed phase. In the case of acidic cobalt maleate monomeric structure is formed, while with neutral cobalt maleate three-dimentional structure is formed (coordination polymer). Structure of metal carboxylate affects their thermal transformations and the properties of metal-containing nanocomposite materials formed. Thus the study of IMHB affecting in molecules of unsaturated dicarboxylic acids (in our case, itaconic acid (IA) molecule) on formation of metal carboxylates is of interest for prognosing the properties of metal nanocomposites, formed by thermolysis of carboxylate. In this study the results of the quantum-chemical calculation of energy of IMHB formation is a molecule of IA are presented.

The calculations were made using GAMESS VERSION 11 AUG 2011 (R1) by DFT method (B3LYP hybride functional with basis 6-31G**). To account for the effect of medium (water in our case) the PCM (Polarised Continuum Model), being one of variations of reactive field model, was used. Calculation resulted in IMHB energy being equal to 7.6 kJ/mol, while lower limit for hydrogen bonds is 4-6 kJ/mol. The IMHB energy obtained is higher than the lower limit for energy of hydrogen bonds and corresponds to weak hydrogen bonds appearing in water solutions of organic compounds.

Then using HyperChem 8.0.8 (Hypercube Inc.) the enthalpy of reaction of acidic and neutral cobalt itaconate was calculated by semi-empirical quantum-chemical method PM3. The calculation were conducted bearing in mind that there is a IMHB in a molecule of IA. The calculations were conducted with account for effect of water medium, and using a cell 14x14x14 Å, in which the molecules were placed. With these dimensions and a mean distance between water molecules being equal to 2.3 Å there were 91 water molecules present. The calculation was carried until gradient less than 0.03 kCal/mol was achieved. It was found that enthalpy of the reaction of forming neutral cobalt itaconate was -234 kJ/mol and for acidic cobalt itaconate – 1340 kJ/mol. The results obtained show us that the formation of acidic cobalt itaconate is favourable in water medium.

Synthesis of cobalt itaconate, carried by us using a water solution, showed that acidic cobalt itaconate $(C_5H_5O_4)_2Co\cdot4H_2O$ is formed. Thus it is shown in present study that quantum-chemical calculations can predict the formation of acidic metal itaconate when synthesis is carried out in water medium.

The work was carried out with financial support of the Russian Foundation for Basic Research (Project No. 13-03-00342).

SYNTHESIS AND THERMAL CONVERSIONS OF COBALT(II) ITACONATE AS A PRECURSOR FOR METALLOPOLYMERIC NANOCOMPOSITES

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Materials based on nanosized particles (NSP) are of wide use in many various areas of chemistry, physics and biology, which stimulates further investigations of numerous theoretical and practically important problems; first of all, the ones about the control of obtaining and stabilisation highly reactive energy-saturated NSP, synthesised in solid-phase processes. During recent years metallopolymers attract greater attention as components or precursors of nanocomposite materials. Among the great variety of metal carboxylates salts of unsaturated dicarboxylic acids (UDA), bearing unsaturated function in addition to carboxylate one, are of especial significance.

The interest to the chemistry of metalloderivatives of UDAs is mostly determined by the practical value of these salts, which are used as coatings with special properties, effective catalysts or drugs. Itaconic acid is a typical member of UDA class, but information about synthesis of cobalt itaconate (CI) and studying its thermal properties is scarce. The goal of present work is synthesis of CI, studying of its thermal properties and conducting thermolysis leading to cobalt-containing nanocomposite and investigating its properties.

Synthesis CI was carried out by interreacting cobalt carbonate with water solution of itaconic acid at 50–60°C. Identity of CI obtained was verified by elemental analysis and IR spectroscopy. Acidic cobalt itaconate $(C_5H_5O_4)_2Co{\cdot}4H_2O$ was obtained. The thermal properties of the CI were investigated using thermogravimetry and differential scanning calorimetry. Thermal conversions was found to include three sequential macrostages: dehydration with simultaneous restructurization of ligand environment; solid-phase polymerisation of dehydrated monomer; decarboxylation of polymeric product formed. Cobalt-polymeric nanocomposite was obtained after controlled thermolysis under argon atmosphere at 335°C for 9 hours. The products obtained were characterised by X-ray phase analysis: in thermogravimetric regime (500°C) the final product was Co_3O_4. Microstructure of thermolysis products was investigated by transmittion (TEM) and scanning electron microscopy (SEM). For automatic processing of electron photographs LabView 8.5.1 was used. Distribution of particle size was determined with a mean value being equal to 21nm. Co-processing of results obtained from SEM and elemental analysis showed the main products of thermolysis under an inert atmosphere to be CoO, $CoCO_3$ and Co_3O_4. Magnetic studies of nanocomposite obtained were carried out: saturation magnetization was equal to 0,52 emu/g, remanence 0,062emu/g, coercive force 451 Oe.

The work was carried out with financial support of the Russian Foundation for Basic Research (project No. 13-03-00342).

SYNTHESIS OF 3D ORDERED MACROPOROUS MATERIALS FOR CATALYSIS AND ADSORPTION

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3D-ordered macroporous (3DOM) materials have found plenty of applications for photonics, biosensorics, size exclusion chromatography, adsorption and catalysis. For the first two application domain structure arrangement is of great importance, while for other fields these materials could be promising from the point of high pore volume with controllable pore size distribution in a wide size range.

For preparation of macroporous structure template-directed synthesis with using of polystyrene (PS) micro- and nanobeads as high-molecular templates seems to be prospective in comparison with other techniques. This approach doesn't require any sophisticated operations, combines with majority of methods for inorganic oxide preparation and provides an affordable template, which is easily obtained and stable as well. Spatial ordering and pore size distribution of the material prepared could be precisely controlled by template dimensions (∅150 nm – 1,5 µm) and arrangement (close-packed or disordered). However, producing polymeric beads with the smaller size, which are especially attractive for catalysis, is still challenging for researchers.

The aim of this work consisted in designing template method for synthesis of 3DOM materials based on Al_2O_3, ZrO_2, TiO_2 and SiO_2 for catalytic and chromatographic applications. For this purpose emulsion polymerization technique was developed to obtain PS beads with the diameter of 90, 130, 180, 250 and 500 nm. Materials were prepared via several pathways: (1) impregnation of the dried template by soluble precursors, (2) direct introduction of precursors into the latex and (3) mechanical mixing of precursors and dried templates.

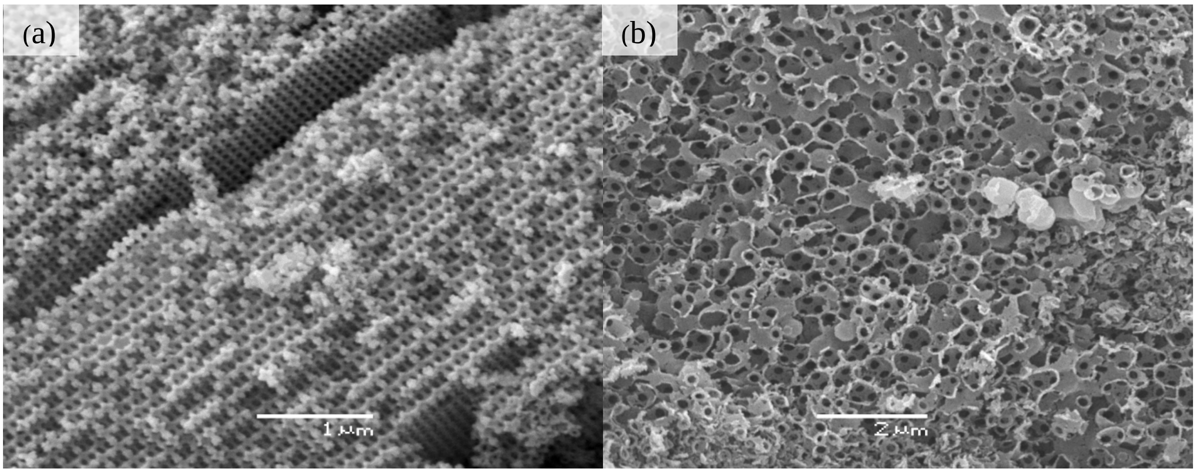

Figure 1. SEM images of macroporous ZrO_2 (a) and TiO_2 (b) samples, prepared by sol-gel synthesis in the presence of PS dried template.

It is worth to be mentioned that design of macroporous structure didn't cancel meso- and microporous texture of the material. As concerns application of structured oxides, catalysts, based on templated Al_2O_3, performed improved activity in heavy oil treating, while macroporous SiO_2 exhibited better efficiency in hydrocarbon chromatographic fractionation.

FUNCTIONAL MATERIALS BASED ON ZIRCONIUM OXIDE

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Our work is focused on a development of physical-chemical backgrounds and methods of controlled synthesis of individual and binary oxide materials based on zirconium possessing a necessary complex of consumer properties and qualities.

The main idea consists of development of methods of controlled synthesis of zirconium low-hydrated hydroxide (LHH) and using of intermediate substances on this basis in synthesis of complex oxide phases.

Low hydrated zirconium hydroxide is the phase with variable composition that contains oxo- and hydroxogroups. Technologically, low hydrated hydroxide is more favourable compared to hydrated zirconium oxide forming gelated precipitates which are filtrated with great difficulties.

The method of controlled synthesis of low hydrated zirconium hydroxide by heterophase interaction ammonia solution with zirconium oxychloride was elaborated. It yields hydroxides with relatively high zirconium oxide content (~70 %), which can be easily filtrated.

These amorphous hydroxide phases possess high reactivity and sorption ability. Physical-chemical properties of LHH of zirconium and products of thermal decomposition have been investigated by using of chemical and thermal analysis, XRDA, IR-spectroscopy and electron microscopy.

The process of thermal decomposition of LHH of zirconium is accompanied by the water removal at the temperature not exceeding $230^{o}C$ and the formation of amorphous phases possessing the highest reaction ability. At the further temperature rise, no other endo-effects which could testify to step character of dehydration was observed. Results of XRD analysis of the condensed phases show, that down to $410^{o}C$ are amorphous, while above these temperatures crystallization of zirconium dioxide occurred. Lattice parameters of the obtained phases have been are calculated. Thus, thermal decomposition of zirconium LHH can be described by the following scheme:

$$Zr(OH)_{1\div3}O_{0,5\div1,5}\cdot 1,4\div2,4H_2O \xrightarrow{200^{o}C} \underset{\text{amorph.}}{Zr(OH)_{1\div3}O_{0,5\div1,5}\cdot 0,02\div0,05H_2O} \xrightarrow{410\ ^{o}C} \underset{\text{monoclin.}}{ZrO_2}$$

High sorption ability of hydroxides allows obtaining the materials at lowered temperatures in comparison with temperatures of traditional method.

The results of investigation were used to synthesis of following phases: $Er_2O_3x35ZrO_2$, $Er_2O_3x27ZrO_2$, $Sc_2O_3x10ZrO_2$, $Sc_2O_3x13ZrO_2$.

OBTAINING OF DOUBLE OXIDES $(Nb_xTa_{1-x})_2O_5$ FROM NIOBOUM AND TANTALUM METHYLATE: SYNTHESIS AND PROPERTIES

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In the modern electronic technology has been a sharp increase in the role of the dielectric and semiconductor materials based on oxides of niobium and tantalum. Using of these materials meet modern requirements such as operational reliability electronics items and development of industrial production of small capacitors, occupying a prominent place in electronic equipment.

Niobium pentoxide and tantalum are the starting compounds for the production of high ferroniobium, nickel-niobium, tantalum and niobium metals. Niobium pentoxide is used in optics. High-purity niobium pentoxide is introduced into the optical glass. Tantalum pentaoxide is used as an optical material in electroluminescent displays.

Niobium compounds pretty close repeat of the same properties of tantalum formations that leads to the idea of the possibility of substitution or addition of one metal to another, It opens a new area of research bimetallic compounds of these metals. This "similarity" in today's increasing consumption of tantalum is fundamental to find substitutes or complements of one component to another. Based on the market value of those metals the price for tantalum pentoxide is higher than the price for niobium pentoxide. So it’s advisable to obtain double oxides of these metals, preserving their properties, allow to extend the field of application, as well as reduce the cost of the initial product.

Niobium and tantalum methoxides characterized by general formula $M_2(OMe)_{10}$ where (M = Nb, Ta) were obtained by electrochemical synthesis. Using these compounds as precursors and using SAS micronization technology oxide powders T-Ta_2O_5 with a particle size of 100-200 nm and oxide powders H(α)-Nb_2O_5 same granulometry can be produced. Sol-gel process was assumed and implemented for production of powders of oxides of niobium and tantalum (V) with a particle size of 1-2 microns using niobium and tantalum methoxide as precursors.

By mixing niobium methylate and tantalum methylate compounds containing two different metals are formed. Their molecular formula $(Nb_xTa_{1-x})_2\,(OMe)_{10}$. Bimetallic solutions were obtained with ratio methylate of metals Nb to Ta as 40:60 and 25:75, respectively. Double oxides with the general formula $(Nb_xTa_{1-x})_2O_5$ were obtained by using SAS method.

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RECEIVING SCANDIUM OXIDE FROM WASTE PROCESSING WET MAGNETIC SEPARATION TITANIUM-IRON-VANADIUM ORES

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One of perspective types of the technogenic scandium raw materials containing rather high concentration of oxide of scandium of 70-140 g/t, waste are wet magnetic separation of iron-titanium-vanadium ores (WMS). Chemical composition of waste of a WMS following, in masses %: 45,02 SiO2, 0,67 TiO2, 8,60 Al2O3, 4,35 Fe2O3, 3,95 FeO, 0,14 MnO, 13,85 MgO, 20,28 CaO, 0,90 Na2O, 0,10 K2O, 0,12 P2O5. Given the distribution of scandium on minerals waste WMS its contents in diopside is 96,64% in anorthite (plagioclase) – 1,87% and in titanomagnetite – 1,49%.

Difficulty of processing of this type of technogenic raw is that the main amount of scandium is concentrated in a strong silicate matrix – diopside, efficient transfer (leaching) of scandium in water solutions demands preliminary destruction of strong crystal structure.

Currently in D. Mendeleev University of Chemical Technology of Russia offered technological scheme of processing of waste of a WMS of Kachkanarsky GOK which includes: mechanical activation processes feedstock, sulfuric acid leaching of scandium in water solution at atmospheric pressure and low temperatures, extraction of scandium from dilute sulfuric acid solutions in the rough scandium concentrate (RSC) and the subsequent processing of RSC with receiving oxide of scandium of high degree of purity.

In the context of the offered technology to exceed the degree of amorphization, mechanical activation samples of a WMS recommended performed using industrial mills of the MP3-MP6 type of the planetary and centrifugal type, let out by LLC “Technics and Technology of Disintegration”. Leaching of the mechanoactivated samples of WMS carry out sulfuric acid with receiving the solutions supporting 6÷12 of mg/l of Sc and 80÷100 of g/l of H2SO4. For extraction of scandium from sulfuric acid solutions offered to use binary extractant di-2-ethylhexylphosphate methyltrioctylammonium (MTOA) followed by solid-phase re-extraction of scandium in RSC. Thus the final content of scandium in RSC reaches 8 %, which corresponds to the concentration of 80 thousand times compared to the initial waste WMS.

Processing RSC invited to conduct on nitrate scheme, according to which the initial RSC is dissolved in nitric acid, followed by extraction of scandium refining using as extractant solution Cyanex 925. Re-extraction of scandium is spent by 20 % ammonium carbonate solution with followed by obtaining oxycarbonate scandium and transfer it in the scandium oxide. For receiving ultra-pure scandium oxide offered to carry out additional stages of extraction or precipitation purification. In the received samples of oxide scandium the total content of metal impurity made 0,075 masses %, and its purity – 99,925% that corresponds to the m3N2 brand according to classification of ALFA Aesar Inorganic Chemicalsand Metals catalog of JONSON MATTHEY.

THE PYROLYSIS MECHANISM OF THE MBH_4–MBF_4 (M = Na, K) MIXTURES

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Thermal dissociation of tetrahydroborates metals $M(BH_4)_n$ (n=1−4 for metals I−IV groups) was devoted quite a lot of researches. The recent paper [1] presents the results of research of $NaBH_4$-$NaBF_4$ mixtures, the pyrolysis of which leads to the formation of $Na_2B_{12}H_{12}$ that there is nothing unexpected [2]. According to [2] the process of pyrolysis of $NaBH_4$-$NaBF_4$ mixtures may be described on following equation:

$$36NaBH_4 + 10NaBF_4 \rightarrow 3Na_2B_{12}H_{12} + 40NaF + 10B + 54H_2\uparrow \text{ (1).}$$

In [1] it presents different:

$$9.5NaBH_4 + 2.5NaBF_4 = Na_2B_{12}H_{12} + 10NaF + 13H_2\uparrow \text{ (2).}$$

To clarify which of the alternative equations true, conducted a number of experiments on pyrolysis mixtures $NaBH_4$-$NaBF_4$ and $NaBH_4$-KBF_4. The reaction products were investigated using methods IR, XRPS, NMR (^1H, ^{11}B, ^{11}B {H}, ^{19}F), and chemical analysis of the $B_{12}H_{12}^{2-}$ anion. The result revealed the following. First, the products of pyrolysis in all cases were painted in a dark colour and their dissolution resulted in the formation of dark brown solutions. This indicates the presence in the reaction products of boron. Equation 2 can not explain this fact. Secondly, a quantity of the generated $B_{12}H_{12}^{2-}$ in the products of pyrolysis of the $NaBH_4$-KBF_4 mixtures was significantly higher than the amount calculated by the equation 1. This can be explained by the fact that NaH, generated by decomposition $NaBH_4$ at the initial stages of the process of pyrolysis can interact with KBF_4 with formation of KBH_4, not of boron:

$$NaBH_4 \rightarrow NaH + BH_3\uparrow \text{ (3)}$$

$$4NaH + NaBF_4 = KBH_4 + 4NaF \text{ (4)}$$

Next KBH_4 condenses with B_2H_6, which supplier is $NaBH_4$. In mixtures KBH_4−MBF_4 (M − Na, K) [3] very high activity KH leads mainly to the formation of boron, i.e. pyrolysis flows mainly under the equation 1. The formation of boron in mixtures $NaBH_4$−$NaBF_4$ can be explained by the decomposition of intermediate on a different scheme than assumed in [1]:

$$2NaBF_2H_2 = NaH + BH_3 + NaBF_4 \text{ (5)}$$

Thus pyrolysis of MBH_4–MBF_4 (M − Na, K) mixtures may go in two directions. The predominance of one or another direction depends on the composition of the concrete mixture.

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PREPARATION OF SORBENTS FROM WASTE PRODUCTS OF DIATOMIT BRICK

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In the manufacture of diatomite bricks a large amount of fine diatomite crumb is obtain. The crumb can be used as filter material. Sorption properties of this material are limited and need to develop technological solutions to improve them.

Sorption properties of diatomite crumbs were studied. The effect of heat treatment on the mechanical and adsorptive diatomite properties was determine.

Using diatomite crumb as a sorbent is demand heat treatment for increase mechanically strong granules. Such granules have been obtained under the action of temperature higher than 400 ° C on diatomite.

To assess the impact of heat treatment on adsorption of nickel ions on diatomite performed the extraction of metals from solution. Value of adsorption was calculated and adsorption isotherms were built . These adsorption isotherms are presented in Fig. 1.

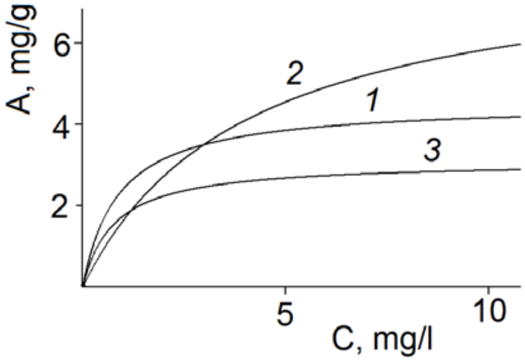

Fig. 1. Adsorption isotherms of nickel ions on diatomite: 1 – without heat treatment; after treatment: 2 – at 400°C, 3 – at 600°C.

According to obtained data heat treatment does not lead to deterioration of the sorption properties of the diatomite. The sorption capacity of the diatomite slightly increased after treatment at 400 ° C (graph 2 on fig. 1).

After heat treatment modifying by chemical or physical methods of diatomite is required for increase the degree of extraction of metal ions. As a possible method of modifying, improving sorption properties of the diatomite sorbent towards heavy metal ions is proposed to use the reaction of acid- alkaline hydrolysis. Hydrolysis leads to intensive extraction of different elements of crystal lattices of clay minerals. This mineral system moves in extremely non-equilibrium condition characterized by high chemical activity. As a result of chemical modification alumino-silicate clay are transformed into finely divided mineral matrix system having a higher sorption capacity by maximizing the sorption- active phases [1].

So as a result of complex processing mechanically durable sorbent with enhanced sorption properties is formed.

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INVESTIGATION OF MACROCYCLIC POLYETHERS AS EXTRACTANTS FOR EXTRACTION OF CESIUM AND STRONTIUM

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Investigation on extraction of cesium and strontium from the complicated chemical composition solutions is an actual task related, primarily, to the processing of liquid radioactive waste. The macrocyclic polyethers (crown ethers) are the most promising of the new generation extractants for extraction and separation of elements with similar properties.

We have previously shown that dibenzoderivatives 18-crown-6 extract cesium markedly from nitric acid solutions and almost don't recover strontium but dicyclohexyl derivatives of 18-crown-6 are effective extractants for strontium. This paper presents the results of research on extraction of cesium and strontium from nitric acid and hydrochloric acid solutions using the most perspective extractants : dibenzo-21-crown-7 (DB21K7), dibenzo-24-crown-8 (DB24K8), 4,4'(5')-di-tert-butyldibenzo-18-crown-6 (DTBDB18K6), dicyclohexyl-18-crown-6 (DCH18C6), 4,4'(5')-di-tert-butyldicyclohexyl-18-crown-6 (DTBDCH18K6). 1, 2-Dichloroethane (DCE) and 1,1,7 - trihydrododecafluorheptanol (FH) were selected from previously studied polar solvents.

Determination of the distribution coefficients of cesium (D_{Cs}) and strontium (D_{Sr}) was carried out by extraction from nitric acid and hydrochloric acid solutions containing 100 mg / L of cesium and strontium and 0.1-5 mol / L acid (HNO_3, HCl) in 0.1 M solutions of crown ethers in organic solvents. Metal concentrations in the initial and equilibrium solutions were determined by atomic absorption spectrophotometry on an AA – 240 FS («Varian») instrument Test Center for collective use of the analytical center JSC "VNIIHT".

Our studies have established that DTBDB18K6 is more efficient extractant of cesium compared with DB21K7 and DB24K8 under the extraction from nitric as well as hydrochloric acid solutions. However, the interesting regularities on the influence of solvents on the process were revealed. Since high D_{Cs} are with extraction from nitric acid solutions in the application FH observed, but D_{Cs} are dramatically decreased when used DCE. The opposite situation is seen in the transition to hydrochloric acid solutions, D_{Cs} are high enough for dibenzoderivatives in DCE, but D_{Cs} are close to zero when used FH as a solvent.

We have high D_{Sr} in the extraction of strontium from acid solutions by selected dicyclohexyl derivatives of 18-crown-6, but it should be noted that DTBDCH18K6 significantly exceeds DCH18C6 on extracting ability.

Dependence of D_{Cs}, D_{Sr} on the concentration HNO_3 and HCl is of an extreme nature, however, the maximum extraction is observed at different concentrations of acid, depending on a solvent and the type of crown ether.

The results can be used for development of the extraction method of isolation and separation of cesium and strontium for reprocessing spent nuclear fuel, and in analytic chemistry.

COAGULANTS OBTAINED FROM KAOLIN CLAYS FROM SUVOROVSKOE DEPOSIT

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In modern conditions, one of the major problems is the protection of the environment, in particular water basin from contamination by harmful substances and rational use of water and mineral resources.

Currently, coagulants obtaining in Russia are essentially of aluminum hydroxide. Therefore, the search of a new resource base for coagulants is extremely important. This paper presents a study on obtaining coagulants – aluminum sulfate and aluminum oxychloride of kaolin clay of Suvorov deposits (Tula region). The chemical and mineralogical compositions were investigated for the samples of kaolin clay. The main minerals are kaolinite (40.0–57.7%), quartz (10.2–33.4%), hematite (4.7–8.1%), maghemite (5.1%), sillimanite (5,1%), grossite (8.2–17.0%).

The basic mineral of clay is kaolinite that without provisional calcination is inert towards acids. Preliminary firing above 500°C increase the decomposition degree of the mineral by acids due to removing of bound water and destruction of its structure with the transition into metakaolinite. During the dehydroxylation occurred phase transition from the structure of kaolinite to mullite structure, decomposition occurs through the formation of silicon spinel, sillimanite and cristobalite. Established optimum calcination temperature of kaolin clay at 600-700 °C to decompose by acids.

Chemical composition of kaolin clay is, %: 30.7 – 34.2 Al_2O_3; 1.5 – 4.5 Fe_2O_3; 47.5 – 50.8 SiO_2; 0.1 – 2CaO. It practically has no harmful contaminants such as Sr, Cr, Cu, Be, Pb, etc., which may have a negative effect on the composition of coagulants and pollute the water. Chemical analysis was performed by atomic emission spectrometry with induction plasma. Al_2O_3 content in the calcination process increases from 32.1% to 38.5%; SiO_2 – from 49.9% to 58.4%.

Investigation of influence of dehydrative calcination – dehydroxylation process of clay on the recovery degree of Al_2O_3 into sulfuric acid hydrochloric acid solutions conducted with varying two parameters: the temperature and duration of calcination.

The calcination temperature varied between 600 and 700°C, the duration of heating to a predetermined temperature was 70-90 min; duration of calcination was 60 to 120 minutes.

Investigated interaction of the calcined clay samples with sulfuric and hydrochloric acids. The resulting samples of calcined clay were decomposing by solutions of sulfuric acid or hydrochloric acid to determine the degree of extraction Al_2O_3 and Fe_2O_3 into solution. For decomposition took a sample of calcined clay in a certain amount (15–30 g). The amount of sulfuric or hydrochloric acid was 102% of the stoichiometric ratio calculated on the interaction with Al_2O_3 and Fe_2O_3. Sulfuric acid with the initial concentration of 92% was diluted with water to an optimal concentration of 20% H_2SO_4, diluted hydrochloric acid is from 37 to 20% of HCl. The temperature of the pulp was 80 to 90°C, the duration of decomposition was 90 min at decomposing in sulfuric acid, 120 min during decomposition in hydrochloric acid. Next, the pulp was filtered on a vacuum filter.

Filtration time averaged 3–3.5 minutes, and with increasing the calcination temperature of the sample, filtration time increased, as the resulting amorphous alumina increases the viscosity of the pulp. The average value of the specific rate of filtration in the experiments was 0,31–0,66 ml/(min·cm^2) or 0.2–0.4 m^3/m^2 · hour, pH ~ 2.5 filtrate.

The resulting cake was dried and weighed, measured volume of filtrate and washings were carried out chemical analysis of solutions and cake. According to the analysis of solutions and cake was determined extraction of alumina into sulfuric acid solutions. The degree of extraction of alumina into sulfuric acid solutions of calcined clay, depending on the duration of the calcination gradually increases, goes through a maximum and then decreases (Fig. 1). With increasing of calcination temperature the recovery rate also increases. The maximum value of extraction degree in a range of 60–90 min at a temperature of 600 °C was 75–80% and at a temperature of 700°C was 87–90%.

The conditions for the extraction of alumina from calcined clay into solutions of hydrochloric acid were also studied. Maximum value at calcination temperature of 600°C – 700°C reached the range of 60–90 min and was 70–73% and at a temperature of 700°C was 76–78%.

Decomposition products of calcined clays are complex disperse system. This system consists of the real solutions of the salts of sulfates or chlorides of aluminum and iron, colloid solutions of silicic acid, silicon salts and solids of undecomposed particles of kaolin clay (corundum, silica, iron minerals). Separation of the liquid or solid phase is a long time process, so to intensify it we recommend using synthetic macromolecular compounds – flocculants. The most widely used for these purposes as a flocculant is polyacrylamide (PAA).

One of the main disadvantages of using natural raw material for coagulants obtainment is a large amount of waste output (siliceous mud). The basic ways of disposing of silica residue is forming of microporite (lightweight building material used in wall construction and thermal insulation products), the use as binder in phosphogypsum, the use as active mineral additives in cement production, obtaining of porous fillers for lightweight concrete (aggloporite), use in the construction and glass production. Si-stoff formed as a fluffy wet mass having water content above 40%. For this reason, transport it over long distances is impractical, mainly si-stoff must be processed on the spot place of production.

SYNTHESIS AND COLLOID-CHEMICAL CHARACTERISTICS OF COMPOSITES "POROUS GLASS-TiO_2"

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The composites prepared by the deposition of titanium oxide structures on various porous matrixes are widely used as catalysts, solid-phase carriers, sorbents, etc. One of the most perspective and modern method of synthesis of such composite materials is a molecular layering (ML) also known as atomic layer deposition (ALD). This method allows to synthesize ultrathin layers of the specified structure and composition with the atomic-molecular accuracy.

In presented work the powders of sodium borosilicate porous glasses (PGs) with an average size of pore channels 20–200 nm were chosen as substrates. Titanium chloride (we used a homemade reactor for the synthesis) and titanium isopropoxide (installation "Nanoserf", Russia1) were used as precursors. The synthesis temperature was 200°C. The number of ML cycles determining thickness of deposited nanostructures varied from 1 to 6. The modification extent of PG particles (external and pore surface) and the changing of their structure and morphology were controlled by methods of electron microscopy2, analytical determination of amount of deposited titania1,3, measuring of specific surface area and pore size distribution1. On the other hand, since functional (sorption and catalytic) properties of synthesized composites are determined by their electrosurface characteristics the electrokinetic potential (laser Doppler electrophoresis) and adsorption of the potential determining ions (dynamic potentiometric titration) were defined in dependence on pH in indifferent electrolyte (NaCl) solutions. Comparison of the isoelectric points (IET) and point of zero charge (PZC) positions, electrokinetic potential (ζ-potential) and surface charge values can be used as an independent control method of the process of chemical surface modification.

It is established that the deposition of titanium oxide layers on porous glass surface results in an appearance of positive region of ζ-potential (at $pH < 4$ whereas pHIET of PGs is approximately 0.5). It should be noted that the growth of ζ–pH dependence slopes for composite structures in comparison with PG substrates was observed. We also observed that IET position for the synthesized composites is between values for the porous matrix and titanium dioxide, the value of negative surface charge of composites is higher than for substrate. Most likely, it can be caused by porosity of the synthesized oxide layers and also essential distinction of properties of nanostructured layers and titania particles. It is shown that extent and uniformity of the modification of porous glass particles are determined by the substrate dispersion and composition and synthesis conditions.

This research used resources of the "Innovative technologies of composite nanomaterials"1, "Interdisciplinary Resource Center for Nanotechnology"2 and "Center for Chemical Analysis and Material Research"3 of Saint Petersburg State University.

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HYDROCHLORIC ACID METHOD FOR OBTAINING OF ALUMINA AND ATTENDANT MATERIALS FROM NORTHERN ONEGA BAUXITE

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The developed technology is based on the acid decomposition of boehmite-kaolinite bauxite in autoclave conditions, which makes possible to reject the pre-calcination of bauxite (complex by technology and hardware), maintaining high extraction of alumina in solution to obtain mother liquors, which can be used as highly effective mixed coagulants feet the regulatory requirements for consumer products, and alumina, which is used in the production of metal aluminum in the process of electrolysis.

As boehmite-kaolinite bauxite were studied rocks from Severoonezhsk deposits, which main minerals are boehmite, gibbsite, kaolinite, goethite (iron hydroxide) and hematite. There are many secondary minerals in bauxite: titanium minerals (ilmenite, rutile, anatase), aluminum (hydromica, hydromuskovite, dickite, feldspar, amphibole, chlorite), quartz, gypsum, carbonates (calcite, rarely siderite), Cr-spinel. Furthermore, it comprises magnetite and sulfides (pyrite – marcasite). As the accessories are present tourmaline, zircon, garnets, kyanite.

Average chemical composition of Severoonezhsk bauxite is next (%): 56,0 Al_2O_3; 15,2 SiO_2; 5,41 Fe_2O_3; 1,08 CaO; 2,73 TiO_2; 0,79 Cr_2O_3; 0,5 S; 1,87 MgO; 16,42 loi. On the basis of X-ray analysis obtained the following mineralogical composition (%): boehmite (AlOOH) – 47,67; gibbsite $Al(OH)_3$ – 9.8; kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) – 27,67; antigorite [$Mg_3Si_2O_5(OH)_4$] – 4,34; hematite Fe_2O_3 – 5,0; Rutile TiO_2 – 2,73; chromite ($FeO \cdot Cr_2O_3$) – 1,20; other – 1.58.

As extract reagent for bauxite treatment used hydrochloric acid solution. In laboratory studies varied duration, temperature of autoclave extraction process, acid concentration.

The experimental technique was as follows: bauxite and hydrochloric acid were charged into the autoclave reactor, which was placed in thermostat where heated at a predetermined temperature and duration of the leach. Pulp mixing provides by rotation of autoclave reactor “over his head”. Upon completion of the experiment the autoclave reactor was opened after cooling for 3–5 min in flowing cold water and liquid phase was separated by filtration from the undissolved residue. The insoluble residue and the mother liquor were analyzed for alumina and iron oxides.

To intensify the process of separating the solid and liquid phases, experiments were conducted on the use of synthetic macromolecular flocculants. Analyzed and summarized results of a study of flocculation properties of organic flocculants, depending on their concentration, the presence of insoluble residue obtained after leaching bauxite by hydrochloric acid. That helps to easy select of flocculant and optimizes technological parameters of its use.

Obtained after thickening, mother liquor was directed to the salting stage. Methods of carrying out the experiment consisted in decreasing the solubility of the aluminum chloride by bubbling gaseous hydrochloric acid through the mother solution. The resulting aluminum chloride was separated from the solution and washed on a vacuum filter.

The crystals of aluminum chloride are subjected to calcination at different temperatures. The resulting alumina was analyzed for content of the main impurities, particle size distribution was measured.

The studies have proved the possibility of production mixed coagulants and alumina from boehmite-kaolinite bauxite by hydrochloric method.

Provided tests in the "RI VODGEO" corresponds that resulting coagulant basic is feet to main requirements in water treatment by color, turbidity, residual content of iron and aluminum.

The certificate of conformity given in the institute FBUN "Federal Scientific Center of Hygiene F.F. Erisman" of Rospotrebnadzor. Analysis and generalization of results of conducted research recommends the use of pedalferic oxychloride for water purification in pilot trials.

THEORETICAL FOUNDATIONS OF ALKALINE CHLORINE AND ACID-CHLORINE METHODS FOR RECYCLING OF ALUMINUM RAW MATERIAL

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Chlorine method at aluminum producing solves two major problems: the expansion of its resource base and achieve an effective energy-saving technology. The raw material for aluminum chloride can serve nepheline, bauxite, kaolin clays, wastes of coal mining and coal beneficiation, shale, etc. The goal of conducted research was to obtain alumina, high reactivity, extracted by alkaline or acidic methods for treatment of non-bauxite raw materials.

Aluminum oxide may be obtained by calcination of aluminum hydroxide extracted in different conditions according to existing methods. For studies used the aluminum hydroxide obtained by carbonizing the aluminate solution at 20 to 80°C and containing no impurities and with sodium hydroaluminosilicates in amounts corresponding to a change in a flint unit (μSi) from 25 to 400; and aluminum hydroxide, obtained by decomposition of the aluminate solution according to the Bayer process. The difference of polymorphic transformations in the test samples of aluminum hydroxide is temperature of the beginning of dehydration and recrystallization. From the thermograms should be taken that the thermal decomposition of carbonized aluminum hydroxide ends at temperatures lower than at extraction by decomposition. X-ray diffraction and crystal-optical analysis methods identified particular polymorphism at dehydration of aluminum hydroxide, depending on the conditions of its formation. It is shown that aluminum hydroxide, extracted by carbonization of aluminate solution at 40°C is represented mainly by bayerite that at calcination temperatures of 600–800°C forms low-temperature modifications: γ-, η- and δ-Al_2O_3; at 800–900°C – high-temperature modification of θ-Al_2O_3 – and at 1000°C – α-Al_2O_3. Decomposed aluminum hydroxide having gibbsite structure and at 600–800°C presented as θ-Al_2O_3 and ǽ-Al_2O_3, and at 800–1000°C – α-Al_2O_3. Thus, aluminum hydroxide, extracted by decomposition of aluminate solutions, the appearance of high-temperature modifications during thermal decomposition occurs at lower temperatures than the carbonized.

Investigated the influence of sodium aluminosilicate and coke (necessary during chlorination) on structure formation of dehydration products. Found that sodium aluminosilicate serves as stabilizer of low-temperature modifications of alumina, expanding existence region γ-Al_2O_3 to 900°C. The presence of coke at thermal decomposition of aluminum hydroxide has amorphized action, ie slows process of alumina recrystallization.

Direct chlorination of nepheline is inefficient due to the large losses of chlorine at formation of chlorides of alkali metals and low reactivity to the chlorine of such alumina. Therefore it is suggested to chlorinate the so-called rough alumina obtained by the developed alkaline chlorine technology of treatment of nephelines from Kolsky Peninsula, according which nepheline sintered with limestone by conventional alkaline technology. Silica-contained aluminate solution is subjected to carbonization at 40°C with separation of the aluminum hydroxide contained of 2,0–2,5% by weight of sodium hydroaluminosilicates, which is subjected to calcination at 700 °C to obtain a rough alumina chlorination is carried out in a fluidized bed furnace at 800–900°C at the presence of a reducing agent – petroleum coke. The resulting chlorides are condensed in the molten salt at 180–200°C and after purification from impurities it directed to electrolysis. Chlorine produced in the electrolysis of aluminum chloride, is returned to the chlorination. Tetrachloride of silicon, separated from aluminum and iron chlorides, is a commercial product.

The alumina can also be obtained by calcination of crystalline hydrate of aluminum salts extracted by treatment of kaolinitic raw materials by acid means. Acid benefication of carbonaceous rocks carried out by sulfuric, hydrochloric and nitric acids. Optimal acid concentrations have been determined for H_2SO_4 – 26%, HCl – 20%, HNO_3 – 40%. The polymorphism of aluminum oxide obtained by thermal decomposition of various crystalline hydrates of aluminum salts brand "chemically pure" and rough alumina extracted by acid benefication of mineral part of carbonaceous rock containing up to 85% kaolinite. The resulting rough alumina contains up to 4% iron oxides impurities and up to 1.0% silicon oxide. Scheme of thermal decomposition of crystalline hydrate of aluminum nitrate and chloride, as determined by x-ray, and crystal studies presented by three distinct stages: in the temperature range 200–600°C – x-ray amorphous substance; further to 900°C formed γ-Al_2O_3, which is a combination of several structural components, and further rising of temperatures up to 1100°C leads to the formation of α-Al_2O_3. Thermal decomposition of sulphate is somewhat different from the previous scheme: x-ray amorphous phase has not been established, the original salt is maintained up to 900 °C and along with it, formed γ-Al_2O_3; above 1100°C – mainly represented by α-Al_2O_3. Presence of petroleum coke and iron impurities has an inhibitory effect on the formation of high-temperature modifications of aluminum oxide.

Chlorination is a heterogeneous process. Kinetics of interaction of the alumina with chlorine at the presence of a solid reductant was investigated in polythermal and isothermal conditions. The rate of interaction with chlorine depends on alumina surface, obtained by different methods from non-bauxite raw materials. The specific surface area was determined by BET method, adsorption of chlorine was studied by thermogravimetric method in polythermal mode from 20 to 1100°C. The highest specific surface area among all oxides had: alumina extracted at dehydration temperature of 700–750°C of carbonized of aluminum hydroxide ~ 350 m^2/g and an alumina obtained by thermal decomposition of aluminum sulfate, ~ 330 m^2/g. The adsorption of chlorine on different types alumina occurred by identical type has two periods of increase in weight of the samples. The first period associated with the physical adsorption of chlorine on the surface of the reactants, followed by exotherm effect and an increase in weight of 2.0-9.0% at room temperature. Second period, arising from chemisorption of chlorine corresponds larger exoeffect and greater weight gain, amounting 6,0–12,0%. At 500–550°C observed a sharp reduction in weight of samples associated with the beginning of chlorination process. Quantity of adsorbed chlorine represents the concentration of surfactants centers of alumina on which begins chlorination process. On the surface of 100 mg of alumina obtained by calcination of aluminum hydroxide at 700 °C, extracted by carbonization of aluminate solution at 40°C with μSi = 40–50 adsorbed 12.2 mg of chlorine, and on the surface of 100 mg of aluminum oxide, obtained by thermal decomposition of aluminum sulfate, adsorbed 11.6 mg of chlorine. This is the best performance. Therefore, investigated structural transformation at dehydration of aluminum hydroxide and the thermal decomposition of different crystalline hydrates of aluminum salts and studied the surface properties of calcined products and defined alumina having the greatest reactivity to chlorine. Direct chlorination of mineral part of carbonaceous rocks is inefficient. Therefore proposed acid-chlorine method of treatment of kaolinite raw material, wherein after the acid benefication and calcination obtain rough alumina, from which, according to the scheme described above, aluminum chloride obtained in fluidized bed furnaces. Offered alkaline chlorine and acid-chlorine methods for treatment of nepheline concentrate in the first case and the mineral part of carbonaceous rocks in the second case focused on the integrated use of raw materials. Feasibility study showed their high efficiency.

STRUCTURAL MATERIALS BASED ON POROUS SILICON FOR MICRO-POWER CURRENT SOURCES

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The development of modern portable electronics is impossible without using of current sources of new generation. One of the promising energy sources are micro-power fuel cells (FC) [1–3]. The most effective power sources for electronic devices are compatible with silicon microchips cartridge hydrogen-air batteries, which can be integrated into various types of electronic devices [1–2].

In comparison with other power sources they have a high functional characteristics – high values of the current density, power, energy density, capacity, wide temperature interval of operation, long term storage. The application of nanoporous matrices-media as a functional substrates will allow us to construct perspective micro-power current sources. In our previous publications it was shown that platinum metal nanoparticles, applied on porous silicon and carbon nanotubes, are effective electrocatalysts for FC [2, 3].

While forming of monocrystalline silicon substrates, by electrochemical anode treatment in the solution of hydrofluoric acid with different current densities was performed. The pore diameter of porous silicon samples was from 5 to 20 nm, with the depth less than 1 μm, and with the various solubilization degree and nanopores form.

Obtaining of nanocomposites was carried out by synthesis of nanoparticles from the solution of the reverse micelles, using Co^{60} gamma radiation as reducing method. This method allows to obtain nanoparticles with high purity and stability, and radiochemical reduction helps to avoid products that can influence on chemical nature of nanoparticles [2, 3]. During the work we obtained the number of solutions with different solubilization coefficient (1 to 8), then the porous silicon samples has been saturated with the subsequent wash and annealing of plates of modified silicon from water-organic phase.

Qualification of composites was investigated by transmission electron microscopy (TEM), scanning electron microscopy (SEM), atomic force microscopy (AFM) and x-ray photoelectron spectroscopy (XPS) and cyclic voltammetry (CVA) method. As a result it was found out that the greatest electrocatalytic activity possess composites which were obtained from water-organic solutions with the solubilization degree 1.5 on the silicon wafers with the porosity 72%. According to microscopy data platinum nanoparticles were discovered not only on the surface, but also in the volume of silicon matrix pores. The average size of the nanoparticles was 4-5 nm. The presence of platinum nanoparticles in the silicon matrix volume contributes to the increasing of stability of catalytic activity during recourse testing procedure.

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Section 5

Polymers and Polymer-Based Composites – Technological Principles and Methods of Synthesis, Modifying and Processing

NANO SORBENTS ON THE BASIS WASTE COAL

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The Institute of Organic Synthesis and Coal Chemistry of Kazakhstan have been developed on the synthesis of different types of humic sorbents for the purification of drinking and industrial water, detoxification and remediation of soil contaminated with heavy metals and to find new effective methods to give them mechanical strength, hydrolytic stability, leach ability and other operational performance by the introduction into their structure of various compounds of organic and inorganic origin.

The paper presents research on obtaining humic nanosorbent based Shubarkol oxidized coal deposits and burned rocks Karaganda coal basin. Considerable deposits of burned rocks their cheapness and availability, high absorbency and filtration properties, durability and the ability to make modifications economically advantageous to use them as a reinforcing matrix to humic sorbents. Burnt rocks are "nanoreactors" with mega-, micro- and macropores, which formed nanostructure. Thanks nanodimensions are significant opportunities to improve the sorption strength and possibly other properties. According to X-ray analysis burnt rocks are aluminosilicates and presented mineral quartz, feldspar, hematite and cristobalite . Studied rocks sufficiently strong and chemically stable, have low acidity and water absorption, porosity between 40% and contains up to 2% of carbonaceous matter.

Nanosorbent prepared by pre activating alkaline rocks with subsequent modification of the activated forms of rock humic compounds at different pH conditions, and the ultrasonic dispersing microwave radiation, the heat treatment at 120–150^{o}C. To modify the used rocks burned humic acid, amino-, sulfo acids and nitro derivatives, as well as polymeric complexes of humic acids with natural and synthetic polymers.

Estimation of the sorption by heavy metal ions held by isotherms in static conditions using methods chelatometry and atomic emission spectrometry with inductively coupled plasma. Physical-chemical characteristics of sorbents were investigated by potentiometers, conductivity, IR spectroscopy, derivatography and radiography. To study the structure and surface morphology of new sorbents and evidence nanostate sorbents involved methods of optical, scanning probe and electron microscopy, nanoparticle size analyzer

The resulting sorbents are materials consisting of activated aluminosilicate which is formed on the surface of the grafted layer of humic acids or their functional derivatives, and polymer. High sorption capacity of sorbents (within 60–98%) is achieved at a low content in their composition of humic component (20–60 mg/g), due to the formation on the surface of the carrier and stable surfactant highly dispersed phase of humic compounds, as well as nano-sized state humic components in the breed. Silica-alumina and its active surface provide a high rate of establishment of sorption equilibrium, low leach ability, high chemical and thermal stability.

SAFETY OF PLASTICIZING COMPOSITIONS AS THE ESSENTIAL TREND OF ECO-POLYMERIC MATERIALS

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Polyvinyl chloride is the second among the largest mass-produced polymers in terms of consumption volumes. Studies on toxicological characteristics of traditional compositions containing mainly phthalate derivatives show that phthalate plasticizers have an effect on human reproduction functions as well as promote a destruction of an endocrine system while high-volatile additives being a part of compositions contaminate workplace air.

The 1990s saw the appearance of a new trend oriented to environmental friendliness of polymeric materials. So-called “green” standards were created and it set stringent requirements for polymeric materials in terms of atmospheric emission of hazardous substances. A control is performed by European Council for Plasticizers and Intermediates; in particular from June 2007 new norms were established (*European regulation REACH7, June 2007*).

PVC goods containing dioctyl phthalate (DOP) were subjected to an expert assessment that revealed their harmfulness for health and consequently it caused prohibition on production and sales of some fast moving consumer goods that contained DOP. Other phthalate plasticizers such as diisononyl phthalate (DINP), diisodecyl phthalate (DIDP), di-*n*-octyl phthalate (DNOP) were acknowledged to be safe and by this reason they may be used in manufacturing of various goods and juvenile products in particular. Dioctyl adipate (DOA) is not only included in the list of safe substances but it is also allowed for food contact goods production. All facts mentioned above are a basis for creation of new and ecologically pure plasticizing compositions.

Following the analysis of a market of plasticizing compositions and keeping in mind the latest scientific researches it was decided to develop a new generation of PVC floor coverings which represent phthalate free floor coverings with “zero emission” of harmful substances. In order to achieve the targeted goals one should apply a totally different approach to the selection of raw materials in terms of chemical composition and toxicological characteristics. It should also be stated that bio plasticizing compositions based on acetic acid ester of monoglycerides made from fully hydrogenated castor oil demonstrated good technical results in the scope of the ongoing project.

Floor coverings based on this plasticizing composition showed not only satisfactory results in terms of physical and mechanical properties but also revealed unique fire safety properties. With this type of plasticizing composition it became possible to eliminate toxic phosphate plasticizers from a formulation and consequently to improve the ecological aspect of a process and a final product.

HIGH-RAPID SILICONE COMPOSITION CURED BY POLYADDITION MECHANISM

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Liquid injection material (LIM) (or liquid silicone rubber – LSR) is widely interested in modern technological processes. Due to the unique characteristics (such as heat resistance, chemical stability, physiologically inertia and electrical insulating) LIM has been extensively used in various industries like aerospace and automobile industry, construction, electric and electronics, medical and food processing industry. In some cases, products from LSR can compete with its metal counterparts.

We set the global task of developing line of LSR production by ourselves, which contains such products as:

1. LSR with the range of Shore 30A to Shore 60A hardness
2. Systems with extremely high and low temperature resistance
3. Electrical Properties elastomers
4. Two-part LSR for molding processes with the short cycle time
5. Optically clear silicone
6. Oil resistance systems
7. Silicone elastomers with the various refracting index (n_D^{20} =1,39 - 1,54)
8. LSR with high tensile and tear strengths

To date, the first LSR composition has been developed. The “Base Compound” for the LSR contain: low-molecular weight polysiloxane with terminal vinyl groups, and an oligoorganosiloksane with the silicon-bonded hydrogen at the ends and / or inside the chain as a crosslinking agent.

Upon heating, the silicone rubber composition cures into a rubbery elastomer. With regard to the curing mechanism of the compositions, the present method can utilize addition reaction types. Addition-reaction types are preferred due to their rapid curing rate and excellent uniformity in curing. (The proses catalyzed by the chloroplatinic acid or the platinum complex at medium or room temperatures.)

The influence of active fillers – fumed silica and treated silica filler as reinforcing additives for LSR was studied. It is shown that by varying the type and content of silica and other filler, using the Base Compound, range of specific materials has been produced.

Based on the laboratory studies, the synthesized LSR have high physical and mechanical properties – tensile strength of more than 3 MPa, elongation not less than 550%, good process ability – pot life ~ 8 h in a mixed state at room temperature (viscosity of the composition within 8 hours, should not change more than 10% of the initial value) and the cure rate ~ 10–20 minutes at a temperature of ≥ 120°C. Introduction inhibiting additives allows composition to remain viable in the mixed state for a long time at temperatures up to 80 ˚C, while the use of pure systems allows curing materials at room temperature, along with the physiologically inertia allows you to use these compositions in dentistry.

Development and implementation of interior LSR production can help to find the solution of different industrial problems, such as: reducing energy consumption and waste production in the manufacture, increment the level of automation, including microelectronics, aviation and automotive industry and other industries – improve the quality of these products, to expand the range and reduce the import of expensive materials.

FEATURES OF THE INTERPHASE PHENOMENA IN HEAT-CONDUCTING COMPOSITES ON THE BASIS OF POLYOLEFINS – NITRIDES – CARBIDES OF METALS

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Interfacial phenomena, greatly changing of physic-mechanical and thermo physical properties of polymer matrix in composite systems depend on the degree of polymer-filler interaction.

Interfacial phenomena in composite systems, polymer inorganic filler can generally be divided into chemical bonding between phases, adsorption and adhesion of polymer chains over particle surface of filler, forming the physic-chemical structure of transition layers in the boundary phase interface, boundary tension of polymer and filler. Thermo physical, electro physical, physic-mechanical and structural features of composites have been used for studying interfacial phenomena in composites based on polyolefin-nitrides-metal carbide.

The degrees of polymer-filler interaction can be judged after studying the posistor thermo-physical and thermoelectric features of composites. Particularly, the given work has researched the temperature dependence of conductivity (σ_k), density (ρ) and thermal-expansion coefficient of composites (α). High density polyethylene (HDPE) was used as polymer matrix, and aluminum nitride (AlN), titanium carbide (TiC) and titanium carbonitride (TiCN) were used as filler of boron nitride (BN).

With the method of differential thermal analysis, for all investigated composites, endothermic and exothermic effects are observed. It is known, that endothermic effect in polymer is conditioned by melting the crystalline phase, and exothermic by depolymerization of polymer chain. Edothermal peak at 403 K and 408 K accordingly occur in thermogram and composite based on it. Temperature changes of endothermic effect formation are considered to be a new crystal forming, under the impact of particle surface filler. It is supposed; that it can appear in phase interface because of polyethylene interaction chains with surface of particles BN, and filler particles is in the role of crystallization centre. Results of the research due to the crystalline degree, temperature and melting heat and composite HDPE +BN shows, that supermolecular features spectra of polymer phase of composite considerably depends on the filler particle influence.

Contribution of interfacial phenomenon in heat transfer through polymer-filler boundaries has been established with complex investigation of thermophysical, dielectric, thermomecanic and structural behaviors (electrical and mechanical). It was established, that electronic properties interphase boundary, the forecast changes of potential barrier volume of polymer-filler contact in composite considerably depend on macromolecular electronegativeness of polymer matrix. Term changes of behavior in interphase boundary with macromolecular electronegativeness changes, the determined concentrated factors which appeared in electric discharge action condition of oxygen-containing group items in polymer chains find their reflection in the volume of potential barrier on the polymer-particle filler boundary.

INFLUENCE OF ELECTRIC DISCHARGE PROCESSING OF POLYETHYLENE ON HEAT CONDUCTIVITY, ELECTRIC AND MECHANICAL DURABILITIES OF COMPOSITES ON THEIR BASIS

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The determination of patterns change in thermal, electrical and mechanical properties of composites from polarity polymeric phase will promote the contribution study of boundary processes in the forming of composite properties, as polarity substantially changes the probability of interfacial phenomena developing and supramolecular structure of the interfacial layer. In this work it is presented the results of a study of composite properties shown above, HDPE + BN, HDPE + AIN and HDPE +TiC (Wt%) received based on HDPE. Then variation polarity of HDPE by treating it in the condition of electric discharge action on the thermal conductivity and physical and mechanical properties of composites. The obtained experimental results show that pretreatment of powdery polymer matrix under the conditions of electric discharges action in air environment at atmospheric pressure leads to increasing of composite conductivity, obtained on its basis. To identify the cause of improving the thermal conductivity of composites, received on the basis of treated polyethylene discharge after the electric discharge machining, had been investigated the changes in the infrared spectra. It was found that after exposure discharges in the IR spectrum PE carbonyl C = O (1700–1750 cm^{-1}) stripes appear, hydroxyl OH groups (3200–3600 cm^{-1}) and double hydrocarbon C = C bonds (1640 cm^{-1}). Thus, the presence of polar groups in the polymer phase is enhanced interfacial interaction, characterized as an increase in time relaxation of the polymer chains in the border of phase sections. The proof of this is the change of current thermal depolarization spectra (TSD) composite HDPE + BN, obtained on the basis of treated HDPE discharge. It was found that in TSD composite spectrum on the basis of treated HDPE is observed conspicuous growth like amplitudes, and the width of the second peak current TSD. It shows that discharge processing increases the concentration of localization charges center, responsible for maximum TSD. The experiments shows that with increasing the concentration of polar groups of the amplitude of the maximum current TSD and λ grow, that indicates the interconnectivity processes of emerging the new centers of particle stabilization , accumulation charge, the formation of strong polar groups and growth the thermal conductivity of the composite.

The comparison of pattern change in the mechanical strength on composite gap from energy discharge processing and ionizing radiation indicates that processing conditions of polymer phase and composite significantly affect the processes, developing both in volume, and at the section border of composite. This is a very important result in the developing of high-effective thermally conductive composites with high physico-mechanical characteristics. In the strengthening of interfacial interaction in composites on the basis of treated by HDPE discharge points temperature depending λ, tgδ and deformation. This effect manifests itself in the temperature growth tgδ, deformation and downturn λ. It should be noted that the electric strength of composites based on pretreated by polymer phase discharge at all filler contents practically equal with electric strength of untreated composites. Thus, the received experimental results indicate a deep relationship between the change under the influence of discharge structure, quantity of stabilized charges, the concentration of polar groups, and the thermal conductivity of composites.

INFLUENCE OF MOLECULAR CHARACTERISTICS AND HETEROGENEITY TO THE KINETICS OF INTERNAL STRESS DURING CURING INDUSTRIAL BRANDS EPOXY OLIGOMERS AND THEIR MIXTURES

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Level of residual stresses in the epoxy oligomers (EO) is defined molecular, segmental mobility fluctuation of nodes and inter-node traffic segments chain (MC), as well as relaxation characteristics, and, therefore, the molecular weight (MW) and molecular weight distribution (MWD) of the oligomer whose weight changes over time in curing. Proceeding from literary data, internal strains of EO defined by a console method can reach ~ 10–12 MPa and more, depending on the mode of curing (heating and cooling).

Studying of strains increase kinetics and level of residual strains during curing of EO depending on various MW, MWD, content of first low molecular weight fraction and the initial structural heterogeneity represents scientific interest. Undoubtedly, it is important to establish a correlation of strains increase kinetics with kinetics of shrinkage, final shrinkage of EO and a theoretical expense of functional groups during curing.

As objects of study chosen EO domestic brands ED-20 and ED-16 (GOST 10587-84), as well as samples of imported brands DER-330 and DER-332 (Dow Chemical), which are almost pure di-glycidyl ether of bisphenol A (DGEBA) (the contents of the first low molecular weight fraction is respectively 92 and 99 wt. %) and their admixtures with adjustable MWD and MM. EO is cured with a liquid aliphatic amine type hardener – triethylene tetramine (TETA) (Dow Chemical), containing two primary and two secondary amino groups, which leads to the formation of the three-dimensional spatial structure in EO at curing. The amount of curing agent was calculated from the equation of epoxy and amine equivalents.

Dependences of increase of residual strains have S – figurative character, characterized by the inductive period (from ~ 1.0 to 4 hours), and the stresses main growth occurs in a narrow time interval (from ~ 1.0 to 10 hours) , reaching its maximum value (σ_{int}) equal to ~ 8 to 12.4 MPa. Maximum values of residual stress (~ 12.4 MPa) were obtained for EO samples with the lowest molecular weight and the highest content of the first low molecular weight fraction – for EO brand DER- 332 (MW = 340 and content of first low molecular weight fraction ~ 99%).

To study the stresses arising in EO is important to take into account the structural aspect, their topological structure at solidification. Residual strains of polymer will greatly depend on the morphological structure of the colloidal level of structural organization, which is largely determined by curing regimen.

The generalized dependences of internal strains on molecular characteristics, conversion and volume shrinkage of EO are for the first time presented.

It is shown that the kinetics and strains level received by the console method is about 8–12 MPa. Found that, with increasing of molecular weight (from 340 to 643 g/mol), the maintenance of associates (about 0.05–0.18 vol. fraction.) and decrease of the content of 1st fraction (1.0–0.8 vol. fraction.) in EO and their mixtures, residual stresses are reduced (from 12 to 8 MPa).

OXIDATIVE ELECTROCHEMICAL POLYMERIZATION OF PLATINUM(II) COMPLEXES WITH AZOMETHENE BASES

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Polymeric films based on transition metal complexes with Schiff base ligands have attracted much interest as their optical transparency, ability to reversible charge transfer, photoelectrochemical activity and some other properties are relevant for the preparation novel materials and devices. The square-planar Pt(II) complexes including those with azomethene bases are the very interesting as potential initial compounds for the electrogenerated synthesis of photoactive and luminescent polymers.

The report presents the new experimental data, characterizing the electrochemical synthesis conditions of stable electroconductive electrochromic polymer film systems based on [Pt(Salen)], [Pt(Salphen)], [Pt(Salpn-1,2)], [Pt(Salpn-1,3)] complexes (where Salen – *N,N'*-ethylenebis(salicylideneaminat), Salphen – *N,N'*-*o*-phenylenebis(salicylideneaminat), Salpn-1,3 – *N,N'*-propan-1,3-diil-bis(salicylideniminat), Salpn-1,2 – *N,N'*-propan-1,2-diil-bis(salicylideniminat). Electrochemical oxidation of the complex was studied by cyclic voltammetry in 0.1 M TBAP/CH_3CN (CH_2Cl_2) using a standard three electrode cell with Pt working and counter electrodes, and an Ag/AgCl (1 M NaCl) reference electrode. Polymers have been synthesized by two procedures: in cycling mode (1-150 cycles) at potential scan rate (v = 0.05-0.1 $V \cdot s^{-1}$) and at controlled potential electrolysis (E = 0.85–1.20 V). Redox switching of the films was made in monomer free electrolyte solution in the potential range 0.0 to 1.2–1.4 V, using scan rates from 0.005 to 1 $V \cdot s^{-1}$.

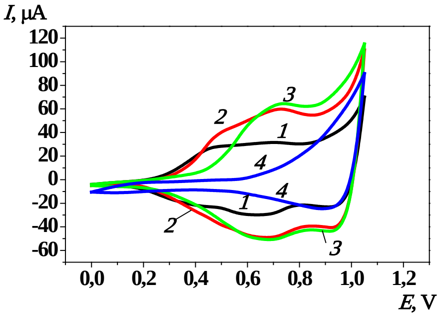

Fig. 1. Typical cyclic voltammograms (2-nd cycle) of poly[Pt(Salen)]-modified electrode in 0.1 mol dm^{-3} TBAP/CH_3CN, between 0.0 – 1.0 V at 0.01 $V \cdot s^{-1}$, prepared by electrode polarization at a potential of 0.9 (***1***), 1.00 (***2***), 1.05 (***3***) and 1.10 (***4***) V for 7 min ($S_{electrode}$= 0.25 sm^2).

It was obtained the polymerization efficiency depends significantly from on the potential range used during polymerization, electrode polarization time and nature of the supporting electrolyte used in electrosynthesis. In the solvent with lower coordination property, CH_2Cl_2, stable films based on Pt-containing compounds can be prepared using a large potential range 0.0–1.3 V, whereas for CH_3CN stable films can only be fabricated using the potential range 0.0–1.15 V. The electrogenerated synthesis rate for all platunum-contaned polymers in CH_2Cl_2 is higher than in CH_3CN. It must be referred also that the all obtained polymers exhibits the oxidation processes shifted 0.1–0.15 V in positive direction in CH_2Cl_2 solutions when compared to its analogous in CH_3CN. It is import the stable fairly thick (≈ 3 μm) conducting polymer phases based on [Pt(Salpn-1,2)] and [Pt(Salpn-1,3)] are formed in CH_2Cl_2.

The photovoltaic positive effect for polymer reduced forms is observed. The maximal values of the photovoltaic effect are 370, 320, 300, 360 mV for poly[Pt(Salen)], poly[Pt(Salpn-1,3)], poly[Pt(Salpn-1,2)] and poly[Pt(Salphen)] respectively.

We have established that the platinum-containing polymer reduced forms are luminescent at T = 77 K.

MODIFICATION OF THE PTFE FILM IN LOW-CURRENT ARGON DISCHARGES

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Modification of a thin film (60 μm) polytetrafluoroethylene (PTFE) in plasma of a low-current combined discharge in argon at atmospheric pressure was carry out. Characteristics of films PTFE initial and modified in the combined discharge are presented. It is shown, that at plasma processing of films PTFE by the combined discharge essentially improve contact properties of polymers.

One of the most effective and technological methods of improvement of contact properties of the surface of polymers is influence low-temperature nonequilibrium plasma [1]. The low-current combined discharge represents the discharge form in which simultaneously in one electrode system it is initiated corona [2], streamer and low-current surface [3] discharges.

Contact properties (contact angles of wetting on water, work of adhesion and adhesion strength) initial and modified in plasma of the combined discharge of films PTFE are presented in table.

Characteristics initial and modified films PTFE

	Contact angle, (degree)	Work of adhesion, (mJ/m^2)	Adhesion strength, (N/m)
initial	104	54,88	95
modified	56	113,6	600

The effective plasma way of updating of a surface of polymeric films is developed for improvement of contact properties of polymers on the basis of the realised combined discharge.

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NANOMETALLOCARBOSILANES AND ADVANCED COMPOSITE MATERIALS COMPONENTS BASED ON THEM

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During the last two decades chemists and material engineers feel particular interest in preceramic polymers and oligomers based on silicon compounds (carbosilanes, silazanes, etc.), which is associated with the development of advanced high-strength ceramic composite materials capable of providing long-term serviceability of products at temperatures up to 1300°C in oxidizing and corrosive environment [1].

In order to create high-temperature ceramic composites capable of prolonged serviceability of the products at temperatures up to 1500–1600°C, the synthesis methods of anoxic ceramic organosilicon oligomers and polymers with metal-containing nanoparticles (Zr, Hf, Ta) – nanometallocarbosilanes [1, 2] were developed.

Synthesized nanometallocarbosilanes possess good fiber-forming properties that allow to obtain silicon carbide ceramic fiber samples, modified compounds of refractory metals (Zr, Hf, Ta). The produced fibers were investigated by modern chemical - physical methods, such as SEM, XRD, etc.

Nanometallocarbosilanes ability to dissolve in hydrocarbon solvents (toluene, hexane) allows their use for the preparation of impregnating compositions intended for the protection of carbon-carbon composites. A feature of the carbon-carbon materials modification by impregnating compositions based on nanometallocarbosilanes is the possibility to introduce silicon carbide modified by refractory metals (Zr, Hf, Ta) compounds to carbon framing that allows the creation of continuous particularly durable ceramic structures throughout the volume of the material.

During nanometallocarbosilanes thermal transformation (pyrolysis under inert atmosphere) silicon carbide nanoceramics modified by metal-containing nanoparticles with a ceramic yield of 70–80 wt. % is formed. XRD revealed that the obtained nanoceramics comprises silicon carbide as the main phase (SiC > 99 %). Crystallite size was D ~ 2nm. The size and distribution of metal nanoparticles in ceramics was investigated by TEM. Elemental composition and ceramics surface morphology were determined by SEM with EDS.

The work was supported by the Russian Foundation for Basic Research (project No. 13-03-12014).

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PREPARATION OF GRAFT AND BLOCK COPOLYMERS OF CHITOSAN WITH ACRYLIC MONOMERS.

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Among polysaccharides – starch, cellulose, chitin which are derived from renewable and virtually inexhaustible sources of plant materials, chitosan attracts special attention researchers. Unique physiological and environmental properties of chitosan such as biocompatibility, physiological activity under the absence of toxicity, biodegradability are causes interest to chitosan. Despite these complex of properties, chitosan don’t have widely accepted in industry. This is mostly due to the low level of physico- mechanical properties of the polysaccharide produced by conventional methods, herewith its degree of deacetylation usually does not exceed 0.8. High physical -mechanical properties inherent to chitosan with 0.92 deacetylation degree, but the synthesis of such polymers requires a significant complicated of the process. Therefore, nowadays the chemical modification of chitosan by polymer synthesis transformations and its copolymers of synthetic vinyl monomers are carried out. The synthesis of graft and block copolymers is promising for improving the physical and mechanical properties of the chitosan, the creation of new materials based on the known monomers with the defined complex of properties. Besides this properties gives variable time of biodegradation polymers, which is important for protecting the environment from plastic waste which is constantly growing.

The aim of this work is obtain the block and graft copolymeres of chitosan and methyl acrylate (MA), 2- ethylhexyl acrylate (2-EHA), 2- hydroxyethyl methacrylate (2-HEMA), 2-hydroxypropyl methacrylate (2-HPMA), N- vinylpyrrolidone (VP), styrene (ST), and research of the complex of physico-mechanical properties.

The degree of conversion of MA, 2-EHA and ST in the copolymerization with chitosan was determined by gas chromatography of the samples of the reaction compound collected at different stages of the process. The concentration of residual monomer was determined by gas chromatography GCMS-QP2010, Shimadzu. To prove the copolymer formation, evaluation of efficiency (weight ratio of graft polymer to the total weight of monomers polymerized) and the degree of grafting (mass ratio of graft polymer to the weight of chitosan) methyl acrylate, 2 -ethylhexyl acrylate and styrene on chitosan was extracted homopolymers MA, ST and 2-EHA from the reaction product using acetone and tetrahydrofuran in a Soxhlet apparatus for 48 hours. The films of the copolymers were prepared by method of pouring. The research of the topography of the film surface was conducted by scanning probe microscopy at atomic force microscope Solver-P47. The influence of copolymer structure on the physico-mechanical properties of the films is ascertained.

It is shown that the conditions of the synthesis of copolymers (pH environment, monomer concentration, temperature and the nature of the monomer) have a significant impact on the composition of the copolymer, and therefore on the physical – mechanical properties of their, which has an undoubted practical value. In addition, block and graft copolymers has different biological stability to microorganisms. Last is important from the economic point of view in exploitation of film materials in various environments. By changing the composition and structure of the hybrid natural synthetic macromolecules the variation of biodegradability could be achieved.

NEW TRIFUNCTIONAL MONOMER FOR ROMP-POLYMERIZATION

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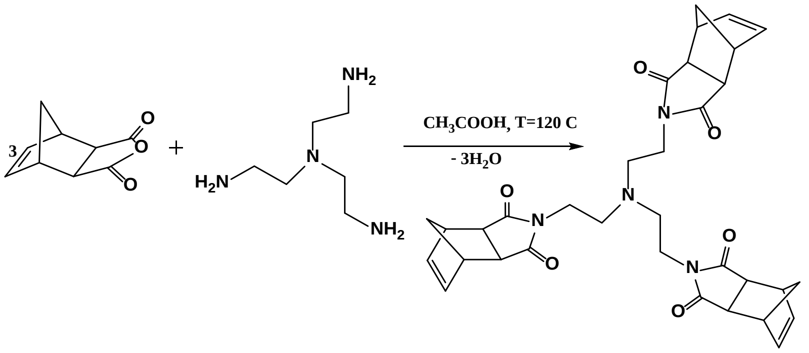
Using the bi-and trifunctional imides as crosslinking agents in the ROMP-polymerization is widely known [1, 2]. By adding of small amounts of these compounds for polymers synthesis by ROMP-polymerization leads to significant changes in physical-mechanical properties of polymers which expanding limits of their applicability. This work was dedicated to the synthesis and identification of new trifunctional monomer (**1**) which active in the ROMP-polymerization. The compound (**1**) was prepared from the exo-norbornene anhydride-2,3-dicarboxylic acid, and tris(2-aminoethyl)amine (fig. 1). It was calculated that $C_{33}N_4H_{36}O_6$ contained C-67,8 wt%, N-9,6 wt%, H-6,2 wt%. The experimental data showed C-67,6 wt%, N-9,3 wt%, H-6,3 wt%. Elemental measurements were performed with Vario MACRO CHNS.



(**1**)

Fig. 1. Synthesis scheme of the new trifunctional monomer.

The structure of compound (**1**) was confirmed by X-ray diffraction analysis. The experimental data is presented in Figure 2.

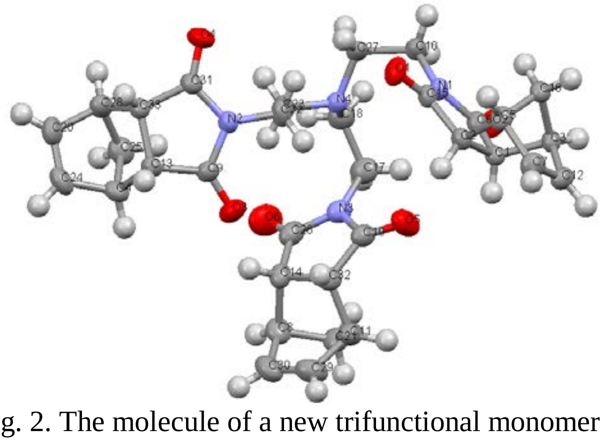


Fig. 2. The molecule of a new trifunctional monomer (**1**).

Therefore, a new compound which can be used as a crosslinking agent in the ROMP-polymerization was obtained in this work.

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SYNTHESIS OF POLY-*p*-PHENYLENE TEREPHTHALAMIDE

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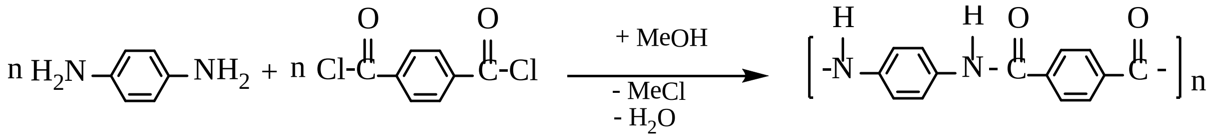
Aromatic polyamides (polyaramids) helped solve the problem of getting light, high-strength, high-modulus, heat-resistant, fire-resistant materials. These materials used practically in all areas of the traditional range of polymeric materials [1].

Poly-*p*-phenylene terephthalamide (terlon, aramid) obtained by polycondensation of an emulsion. Aramid reaction equation:



The apparatus consists of a 3-necked flask equipped with a mechanical stirrer, water condenser, dropping funnel and oil bath.

Investigated the effect on the polymer yield and molecular weight:

a) investigated the influence of reaction temperature on the yield and the molecular weight of the polymer;

b) the effect of various hydrogen chloride acceptors – low molecular weight reaction product.

a) Aqueous phase – 0.1n solution of *p*-phenylenediamine and 0,14 n sodium hydroxide solution. Organic phase – 0.1n solution of terephthaloyl chloride in toluene. The process was carried out at various temperatures – from 25 to 95 °C.

Analysis of the dependency showed that the molecular weight (reduced viscosity η_{red}) and the polymer yield almost linearly increases with the temperature of the process.

The absolute value of the viscosity obtained at a temperature of 25°C, corresponds to the industrial designs ($\eta_{red} = 3{,}9\cdot10^{-2}$ m^3/kg). But under these conditions, we have a low yield polymer. Maximum molecular weight corresponds to the highest output (ε = 72%) at a process temperature of 95°C. The dependences obtained are consistent with the literature data.

b) the organic phase – 0,1n solution of terephthaloyl chloride in toluene. Aqueous phase - 0.1n solution of p-phenylenediamine and 0,14 n alkaline solution (Na_2CO_3, KOH, NaOH). Temperature of synthesis – 95°C.

Influence of the hydrogen chloride acceptor species on the yield and the molecular weight of the polymer is uniquely. Maximum values (η_{red}) detected by using sodium hydroxide. Use of sodium carbonate as a scavenger of low molecular weight reaction product is inapplicable: low yield (ε = 22%) and molecular weight ($\eta_{red} = 0{,}4\cdot10^{-2}$ m^3/kg).

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THE SEMI-DRY METHOD OF SYNTHESIS OF HIGH-SUBSTITUTED CATIONIC STARCHES

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One of the most demanded derivatives of starch – cationic starch is synthesised now mainly in water suspension that demands the big expenses for technological equipment of an industrial line and the big expense of water both for carrying out of the reaction, and for the subsequent washing a ready product. Recently the gradual tendency of transition to «semi-dry cationisation» - to carrying out of reaction with a water minimum quantity is observed. Thus it is possible to result many arguments which support use of this method of synthesis:

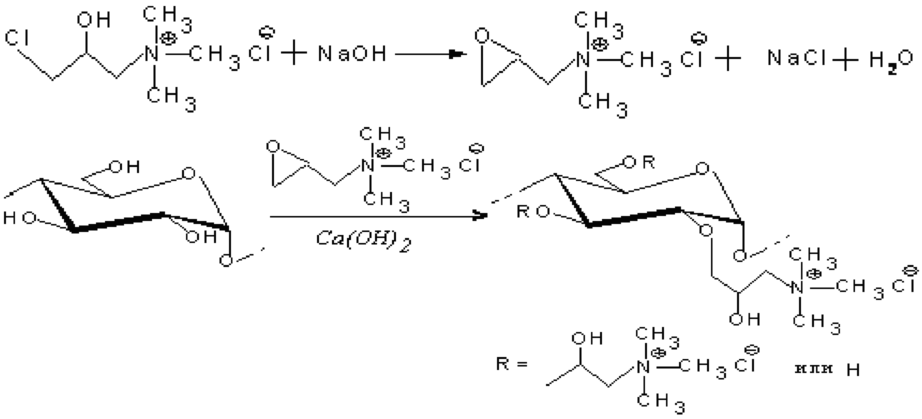
- higher efficiency of cationisation reaction and reception possibility cationic starches with higher degree of substitution (to DS = 0,5) as with increasing DS cationic starch becomes more soluble in cold water and its allocation at synthesis in water suspension leads to considerable problems;

- the minimum losses of starch and elimination of problems with sewage, as result of absence of a stage of washing (ecologically more safe process);

- smaller expenses for equipment of a technological line and minimum time of finding a reactionary mix in a reactor (0,5–1 h at «semi-dry cationisation» against 8–24 h at reaction carrying out by slurry process);

- the absence of necessity of use salts and economy of energy as reaction can be spent at a room temperature.

The general scheme of reaction of the semi-dry cationisation on the developed way can be presented as follows:



(1)

(2)

The during the spent researches laws «semi-dry cationisation» of potato starch with use 3-chloro-2-hydroxypropyltrimethylammonium chloride and catalysts $Ca(OH)_2$ and NaOH have been studied. It was established, that the content of cationic groups in an end-product and reaction efficiency depend on the water maintenance in a mix and also from molar parities starch: catalyst: 3-chloro-2-hydroxypropyltrimethylammonium chloride.

The synthesized high-substituted cationic starches unlike low-substituted one are dissolved in cold water and can find wider application. The possibility of use of samples cationic starches as effective flocculants which are not conceding by the efficiency widely applied flocculants on a basis polyacrylamide and its derivatives was shown on modeling systems of the caolin dispersions.

COMPLEX COMBINATIONS OF TRANSITIONAL METALS WITH REDOXYLIGANDS – NEW TYPE CATALYST IN HYDROSILICATING REACTIONS OF UNSATURATED SILICOORGANIC MONOMERS

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The catalyst is one of the most important component vulcanizing systems, allowing influence upon velocity of the vulcanizing, nature of the forming net, temperature and hardening depth, as well as allowing to obtain compositions with the necessary set physical-chemical features.

In observed work catalysts of the fundamentally new type were synthesized - complex compounds of the platinum group with redox-ligands, capable to monoelectronic reverse transition – bensonytril-type complex compounds of platinum, palladium and rhodium.

The electrochemical characters and velocity of the complex obtained interaction with a classical hydroxylate reagent – hydrid-containing silans, vinilsyloxans, were studied. The compositions, basing the vinilsyloxan rubbers, hardened with the complex of platinum with redox-ligands, give the small reconstruction peaks. The smaller eduction of the hydrogen occurs at cation-radical – sylan fragmentation in comparison with the traditional catalyst (the systems based on platinum – a Spayer catalysts).

It is shown for the first time that the role of the catalyst is to generate catyon-radical low-molecular sylan, the further fragmentation of which leads to throwing out of atomic hydrogen and forming the siliconium ion. The reaction hydrosylating runs by furcated chain reaction mechanism, platinum anode – an initiator of the chain reaction.

The complex compounds of metal platinum group with redox-ligands - high viability, vulcanizing velocity, high dielectric parameters; low temperature hardening (900 - 600C) compositions are obtained under usage of high active catalysts synthesized. The main advantages of catalyst synthesized are its reusability; lack of mixture spontaneous heating and temperature leap – important for industrial conditions.

Noted that new hydrosilating catalyst – rhodium semiquinolate, – does not cause the metallic article corrosion.

The physical-mechanical and electrical features of the polymetil-vinilsyloxan composition designed under accelerated vulcanizing are following:

- conditional toughness, MPA – 1,5–5,0;
- relative lengthening – 100–150%;
- elasticity module, MPA – 1,7–2,2;
- dialectical losses tangent at frequency 10^6 Hz – $5 \cdot 10^{-4} – 3 \cdot 10^{-3}$;
- dialectical permeability at frequency 10^6 Hz – 3–3,5.

The correlation between electrochemical data and rubber hardening will allow offering the scientific foundation for search of new effective, selective and sufficiently available catalyst to polyconnection reactions.

The complexes synthesized so as materials designed on their fundament will find use in the electronic technology items.

THE PENOPOLYOLEFIN'S MODIFICATION WITH FILLERS OF THE VARIOUS NATURE

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Recently Gas-filled polymers are widely used in various branches of a national economy. Polyethylene foam takes a special place among these materials. Inspite very low prime cost of the raw materials and the estimated low prime cost of received products. The technology of receiving polifoams from poliolefins appeared much later similar technologies for other polymers.

Currently penopoliolefins are the most roughly developing sector of the receiving gas-filled polymers. This is facilitated by a combination of low cost and high performance characteristics and chemical resistance. At the same time, this material has a number of disadvantages that high flammability, high creep of the material and in some cases insufficient rigidity.

The analysis of literature showed that fillers of various nature can be used for reduction of these disadvantages. The purpose of this work is research of possibility of introduction in composition a filler of various nature (disperse, fibrous, hollow spheres, etc.), determination of optimum concentration of a filler and determination of properties of received products.

The disperse fillers (chalk, talc, a marble crumb, a kaolin) and the fibrous (glass, basalt fibers) were investigated as a fillers. As a result of the done work it is shown that without changing technology it is possible to enter into composition till 40-50 masses. p. filler on 100 masses. p. polymer.

It is established that all input fillers reduce creep and increase physico-mechanical properties of initial polyethylene foam. It is shown that the introduction of fibrous fillers primarily of the basalt fiber with increased tensile. strength of more than 40% is almost unchanged apparent density.

By methods of IK-spectroscopy it is shown that difference of properties of carrying out glass and basalt fiber is connected with that a chemical interaction of a polymer's matrix to a fibrous filler (basalt) is in the course of receiving the made foam material. Thus, the possibility of introducing a filler of different nature without changing the technology of foamed polyethylene foam with simultaneous increase of their strength properties is shown.

HYPERBRANCHED POLYIMIDES BASED ON TNT DERIVATIVES

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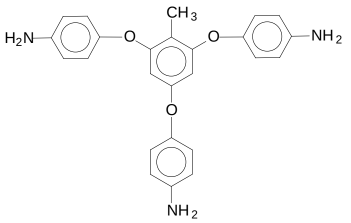
In earlier works of Rusanov and Shevelev with collaborators [1], several directions of chemical transformation of trinitrotuluene (TNT) was offered. More specifically, TNT amino derivatives were successfully used the monomers for linear polyimide soluble in organic solvents.

In this work, we demonstrate possibility of use 2,4,6-*tris*-(4-aminphenoxy)-toluene (TAPhT, monomer B3, product obtained from TNT derivative – metylfloroglucine), as starting material in synthesis of hyperbranched polyimides (HBPI) using scheme (A2+B3). TAPhT is 3-functional reagent. Corresponding tris-phthalimido-derivative Tm = 240°C was obtained with the yield of 95% in the model reaction – the high temperature condensation of TAPhT with phthalic anhydride in molten benzoic acid (BA) at 140°C for 2 hours. This result confirms reactivity of all three amino groups in TAPhT.

Sample of HBPI was synthesized by the one-pot high temperature polycondensation (HTPC) of B3 with 2,2-bis [(3,4-dicarboxyphenoxy)phenyl]propane dianhydride (BPADA) as monomer A2 at 140°C. HBPI with amino terminal groups was obtained at molar ratio A2/B3 equal 1/1. A2 was steadily added to B3 for 45 min. After addition of A2 was completed, reaction was mixed at 140°C for 2 hours. BA was extracted from the mixture by washing with diethyl ether. Product was evacuated as brown amorphous powder soluble in CH_3Cl, THF, DMFA, DMSO. Logarithmic viscosity is 0,29 dl/g. ($CHCl_3$), Tg = 198°C (DSC). It was characterized by means of FTIR(CsI), ^{1}H and ^{13}C NMR (dmso-d6) and GPC (THF as eluent). Product evacuated has wide molecular weight distribution (1000-100000 Da).

HBPI with terminal anhydride groups was synthesized using molar ratio A2/B3 equal 2/1. B3 was steadily added to A2 for 45 min. After addition of B3 was completed, reaction was mixed at 140^0C for 2 hours. Final product was washed by diethyl ether. Product was evacuated as light-brown amorphous powder soluble in CH_3Cl, THF, DMFA, DMSO. Logarithmic viscosity is 0,23 dl/g. ($CHCl_3$), Tg = 191°C (DSC-data). It was characterized by means of FTIR(CsI), ^{1}H and ^{13}C NMR (dmso-d_6) and GPC (THF as eluent). Product evacuated has wide molecular weight distribution (1000–100000 Da).

Thus, new hyperbranched polyimides with terminal amino and anhydride groups were successfully synthesized from TAPhT. Such type of HBPI are of interest for many applications including optical materials, gas-transport membranes etc.



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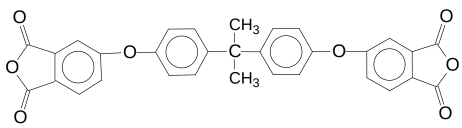

A_2

The work was supported by RFBR, grant No. 10-03-01041a.

Reference:

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PREPARATION OF THE NEW POLYMERS BY USING RING-OPENING METATHESIS POLYMERIZATION

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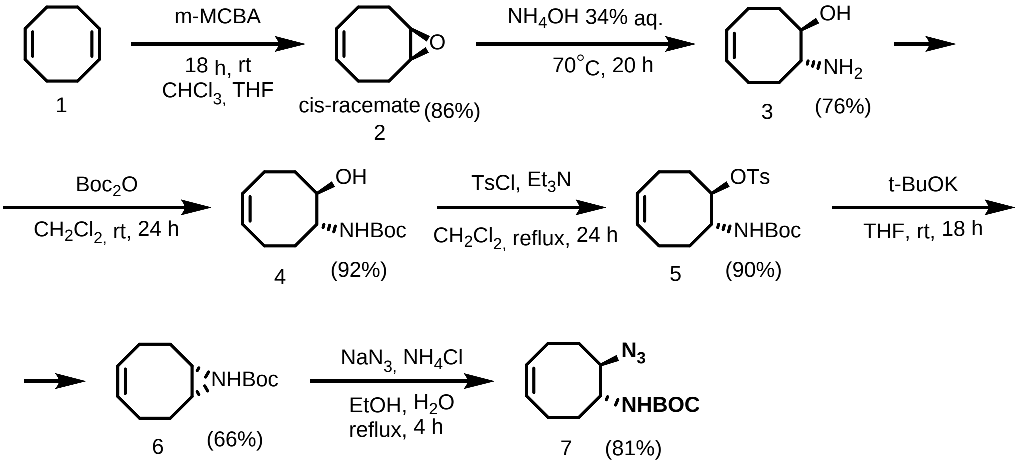
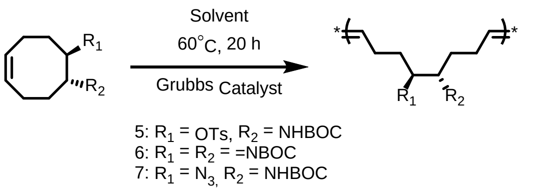
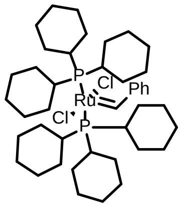
In this study, we investigated the ring-opening metathesis polymerization (ROMP) of cyclooctene derivatives using the commercially available catalysts and demonstrated a facile and general strategy to prepare functionalized oligo(cyclooctene)s in excellent yields.

The scheme below shows the synthesis of 5,6-substituted cyclooctenyl from commercially available cyclooctadiene **1**. Compounds **5**, **6** and **7** were used as the monomers for the (ROMP). As metathesis catalysts were used catalysts Grubbs and Hoveyda-Grubbs generation 1 and 2. DMF, CH_2Cl_2, and toluene were used as a solvent for ROMP. Reactions were carried out at 60˚C in closed vials under argon.

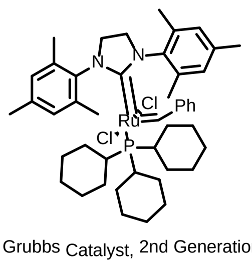


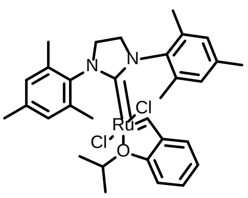
In the polymerization of compound **5** under different conditions were low reactions yields of polymers because the monomer and polymers are not stable. Polymerization of monomer **6** results to polymers of low molecular weight (under 1500). Polymerizations of monomer **7** were obtained polymers with quantitative yield and high molecular weights.

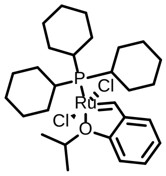




Grubbs Catalyst, 1st Generation







Grubbs Catalyst, 2nd Generation Hoveyda-Grubbs Catalyst 2nd Generation Hoveyda-Grubbs Catalyst 1st Generation

MESOPHASE BEHAVIOR OF BINARY MIXTURES OF LIQUID CRYSTALLINE ACID

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Liquid crystals are truly fascinating materials in terms of their properties, importance for the fundamental understanding of molecular self-assembly, and their tremendous success in commercial applications. These unique materials combine order and mobility. Liquid crystals prepared by self-assembly processes via formation of intermolecular interactions such as hydrogen bonding, are promising materials for fabrication of new functional materials. Alkoxy benzoic acids is liquid crystals formed by hydrogen bonded molecules and successful are used as quasi components.

A series of binary mixtures of homologues of 4-alkoxy benzoic acids bearing alkoxy groups with different chain lengths, were prepared from the molten state and their mesophase behavior investigated by POM, DSC. The results showed that most of the mixtures are dimorphic exhibiting the SmC and N mesophases. Referring to the mesophase stability, it has been shown that the increase of the average alkoxy chain length in the mixture increases, as expected, the thermal stability of the SmC increases and that of the N phase decreases. The binary phase diagrams of acids bearing different alkoxy-chain lengths indicated that molecular length plays an important role in the formation of new liquid crystalline complex. So systems with close in length terminal substituents tend to the formation of supramolecular complex, but mesogens strongly differing in molecular length take place cocrystallization.

Hydrogen bonds promote the formation in the systems of additional nematic subphase. The transition from N'' to N' is ascribed to the growth of cybotactic clusters having short-range smectic order in the nematic phase under a certain temperature. This means that in the nematic melt, if the temperature is low enough, the closed dimers can aggregate in clusters with smectic C ordering. In N'', the local smectic order of the cybotactic clusters is destroyed by the high concentration of monomers and open dimers. Transitions between subphases are recorded in the entire composition of only using PPM.

The results have been obtained within the framework of State task of the Ministry of Education and Science of the Russian Federation.

THE SYSTEM OF PROCESS AND STRENGTH PROPERTIES SECONDARY HDPE USED FOR ECONOMY CLASS SEWER PIPES

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Increased construction and repair of pipeline networks, including sewage, has increased the demand for HDPE pipes.

According to GOST 22689.2-89 pipe intended for internal drainage systems of buildings are made of high density polyethylene (HDPE) and low (LDPE) with a pressure of not more than 2 MFI g/10 min.

The high cost of raw materials leads to the need to expand the resource base without compromising the quality pipes, primarily through the use of secondary polyolefin. But there is currently no real characteristics of secondary plastic raw materials, produced by different manufacturers are often mixtures of secondary HDPE with of secondary LDPE or of secondary PP, and data on their compliance with the requirements for pipe grade HDPE.

In this work carried out a comprehensive evaluation of the properties of 27 samples of secondary polyethylenes produced the largest Russian manufacturers.

Determining the type of polyethylene and thermal stability-oxigen index (OI), carried out at 200°C by DSC, rheological properties were studied by capillary rheometer firm LCR 7001, MFI – according to GOST 11645, molecular weight characteristics of the samples were determined by gel permeation chromatography.

Identification of samples by DSC analysis showed that only 6 of them are secondary HDPE or mixture of secondary HDPE with of secondary LDPE with the remaining samples contained PP. Therefore, a more detailed analysis of the properties was carried out for 6 samples SHDPE (a blend of 80% of SHDPE and 20 % of SLDPE, a blend of SHDPE 276 and SHDPE 273, SHDPE 01030, SHDPE in form of white flakes, flaked SHDPE 6949 and pelletized SHDPE 6949).

Determining MFI showed that similar values with 2NT11 PE100-9 (0.15 g/10 min), only for sample SHDPE 6949 (pelletized – 0.15 g/10 min, flaked – 0.27 g/10 min.) MFI samples of the mixture of 80% of SHDPE and 20 % of SLDPE, a blend of SHDPE 276 and SHDPE 273, SHDPE 01030, SHDPE in form of white flakes ranges from 0.58 to 0.68 g/10 min, which is higher than the value for HDPE used for extrusion of pipes.

In terms of thermal stability (OI) only the two samples HDPE 6949 to meet the requirements of the tube makes (at least 20 minutes).

Rheological studies have shown that the flow curves for samples of flaked SHDPE 6949 and pelletized SHDPE 6949 differ greatly from flow curves of other samples. Since flow index (n) of samples of flaked and pelletized SHDPE 6949 at shear rates from 0.6 to 2*102 s^{-1} is equal to 0.25 and 0.29, while the remaining samples – 0.43. At a shear rate of 2*102 s^{-1} flow index samples SHDPE 6949 drops to 0.2, and for the remaining samples did not change. For 2NT11 PE-9 n = 0,25. The reason for the differences rheological characteristics of the secondary high density polyethylenes is a significant difference MWD and branching patterns.

Samples of SHDPE 6949 are characterized by a broad distribution of MW. (MWD power 21.4 and 26.4, respectively, for a blend of SHDPE 276 and SHDPE 273, a mixture of 80% of SHDPE and 20 % of SLDPE and SHDPE 01030 – 15.4, 15.8 and 14.2, respectively). 2NT11PE -9 - MWD = 12.94.

Thus, the use SHDPE for producing sewer pipe requires constant provider to guarantee the absence of other raw materials of other polyolefins, corrections of process parameters on the entire line of extrusion due to the difference of rheological behavior of primary and secondary raw materials caused by the difference of the molecular-mass characteristics. More appropriate is the use of technological waste of its own production.

SYNTHESIS OF THERMOPLASTIC POLYURETHANE IN ROTOR TYPE MIXERS

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Structure formation processes and properties of thermoplastic polyurethanes due to them may be presented as follows. At room temperature, flexible segments with low glass transition temperatures become incompatible with polar hard segments having high glass transition temperature, which leads to a microphase separation. Partially the driving force of the single-pole separation process is caused by the hard segments crystallization process that takes place. When heated to a temperature above the hard segment melting temperature the polymer forms a melt of relatively uniform viscosity, which can still be processed using such thermoplastic processing techniques as injection molding, extrusion, blow molding, etc. Subsequent cooling leads again to the separation of both rigid and flexible segments and to restoration of elastic (resilient) properties. Thus, during the synthesis of thermoplastic polyurethane there should be provided conditions for establishing such a chemical structure that would allow for achieving the most complete microseparation of phases.

Effect of temperature, catalysts and components addition sequence on the thermoplastic polyurethane ability to microphase separation was studied using a Brabender plastograph.

Investigations of the properties of polymers produced by different synthesis routes (with simultaneous and stepwise components addition) were studied. A conclusion was made that undesirable route of thermoplastic polyurethane synthesis may be avoided by using an intermediate pre-polymer formation stage by a polyol reaction with a diisocyanate. When estimated amount of diisocyanate is added, isocyanate-terminated pre-polymer is formed, and in case of partial addition, diisocyanate is mainly used to form "bridges" with terminal hydroxyl groups, and thus a pre-polymer with terminal hydroxyl groups is formed.

By the nature of plastogramms recorded during polymer synthesis end product properties can be accurately evaluated. It was found that the stepwise addition of components is most preferable, and it is efficient to synthesize polymer in the apparatus like a Brabender plastograph. Research-based recommendations regarding implementation of thermoplastic polyurethanes synthesis were worked out. The rotor mixer design was developed, which provides for the possibility of carrying out the synthesis at relatively low temperatures. Polymer homogenization is achieved due to the use of worked out rotors apex design that provides for the head-on mass feed at an angle of 90° to the rotor axis. By means of it, when two streams meet, stress "stretching" polymeric macromolecules along the rotor axis is formed again and again. Properties of thermoplastic polyurethanes produced using rotary mixers with tangential melt flows direction were studied.

INVESTIGATION OF PROPERTIES OF CELLULOSE ACETATE BASED BIOCOMPOSITES

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The term "bioplastics" is associated not only and not just with the fact that this material is produced from renewable biological resources. Most often, bioplastics, particularly cellulose acetate plastics, are seen as materials with low strength characteristics which are unsuitable for the structural materials manufacture. This is due to the fact that bioplastics are operable in a narrow temperature and mechanical stress range. However, cellulose acetate plastic chemical modification research suggests that their use as structural materials may be environmentally and economically sound direction for the polymer technology development. Moreover, it is expected that chemically modified cellulose acetates (unlike ungrafted polymer) are technologically compatible with synthetic polymers. Thus, joint regeneration of bio- and synthetic polymers will be possible. Analysis of literature data and results of studies carried out by the authors showed that the method of condensation grafting is the most promising method for the chemical modification of cellulose acetate. Whereas, during radical copolymerization and polycondensation grafting uncontrolled amounts of homopolymers and residual monomers are formed. In this study, chemical modification of cellulose acetate was carried out using oligoester and a diisocyanate based oligomer.

The average degree of substitution of cellulose unit cells hydroxyl groups was 2.5. Samples of cellulose acetates modified using various oligoester/diisocyanate concentrations were prepared at 180°C in a rotary Brabender plastograph with a nominal chamber volume of 30 cm^3. The effect of oligoester/diisocyanate concentrations on chemically modified cellulose acetate properties was studied. Degree of grafting (crosslinking) was evaluated based on reducing the solubility of the samples obtained and by compositions melt viscosity increase. Test samples were prepared at 180°C in a hydraulic press under compression molding pressure of 2.0 MPa. Experimental batches of optimum compositions were prepared at Buss oscillating mixer, and test samples – using laboratory injection molding machine with a clamping force of 10 tons and a maximum casting weight of 20 grams. Change in parts appearance, heat resistance and mechanical properties were monitored. With the oligoester/diisocyanate concentration increase chemically modified cellulose acetate melt viscosity increases while the solubility in acetone and dimethylformamide decreases. According to those indicators the molar ratio of 1:1 is a critical value.

POLYVINYLCHLORIDE'S POLYFUNCTIONAL DISPERSE FILLERS BASED ON TECHNOGENIC RAW MATERIALS

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Polyvinylchloride is characterized by low heat stability and high molten viscosity. Creating polymer compositions it is appropriate to use fillers combining polyfunctional effect and securing improvement of technological, service and technical properties. Fillers that increase heat stability and at the same time reduce molten viscosity at processing stage and cause novel properties or escalating available properties are required first of all. Disperse technogenic raw materials in polymer constructional materials may be used instead of high-priced fillers. Requirements of mineral, chemical and material composition for polyvinylchloride materials modification are identified in this research. To realize polyfunctional principles in our research considerable attention was paid to waste containing a variety of functional groups. Analyzing them we formed the classification of fillers that positively affects such properties as heat stability and molten viscosity:

- it was established that fillers with pH-factor 7-8 are appropriate to provide acceptance of hydrogen chloride that releases at destruction of polyvinylchloride;

- fillers wetting energy value by plasticizer (dioctyl phthalate) at standard conditions is determined (-0,08 J/g) which determines flow behavior index of polyvinylchloride compositions.

Explored waste could be ranged by the efficiency of complex positive affect (increasing heat stability, reducing molten viscosity, upgrading rupture resistance, water absorption decrease).

It was established that fillers with complex material composition owing to combination of different types of thermal PVC stabilization possess internal synergetic effect. Mineral component is a hydrogen chloride acceptor, organic component is antioxidant.

Wastes that contain hydrophobic organic components less than 5% are composition's conformational plasticizers. Usage of these conformational plasticizers allows to reduce molten viscosity by about a factor or two.

CARBON NANOTUBES MODIFIED WITH THE SURFACTANTS – AN EFFICIENT REINFORCING ADDITIVE FOR POLYMER COMPOSITES

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The creation of lightweight polymer composite materials with excellent specific mechanical properties reached by carbon nanostructures (carbon nanotubes, fullerenes and graphene) inclusion in polymer matrix is a prominent area of current research and development in modern material engineering and polymer science. Carbon nanotubes (CNT) is a high-potential material for a variety of applications due to their remarkable mechanical, electrical, physical and chemical properties. General problem is the tendency of nanotubes to aggregate as a result of van der Waals forces and hydrophobic interactions. For efficient polymer nanocomposite reinforcement a homogeneous distribution of isolated individual or small aggregates of carbon nanotubes in matrix is required. So, the development of carbon nanotubes dispersing technology in liquid media is of great technical importance. The results of current investigations shows, that noncovalent CNT surface modification has the advantage in preserving their remarkable properties, and CNT have been successfully dispersed in liquid media with the aid of a vast number of different dispersive agents, such as surfactants. The preparation of stable homogeneous CNT dispersions based on nonionic surfactant solubilization of carbon nanotubes is a promise area of recent study [1, 2].

The main purpose of this work is the investigation of nonionic surfactants ability to CNTs disaggregation and stabilization. The ingredients of composites formulation – solvents, softeners, oligomers, interfacial compounds and adhesive compositions were used as the dispersive liquid media. We have studied the influence of amphiphilic compounds – nonionic surfactants (alkylene oxides block-copolymer, silicone surfactants and nonylphenol ethoxylates with various ethoxylating degrees) on the colloidal properties of CNT dispersions. A choice of the surfactants was based on the results of our previous works concerning the interaction between amphiphilic compounds and polymers in the processes of polymer materials production [3].

The conditions of CNT dispersions obtaining by means of ultrasonic treatment were developed. The content of CNT in liquid media was measured by absorption spectroscopy. Dispersions structure was examined by confocal microscopy and dynamic light scattering methods before and after centrifugation. The degree of nonionic surfactants adsorption on CNT surface was defined by surface tension measurements. Silicone block-copolymer was established to be most effective dispersing agent. The optimization of colloid and chemical properties of CNT dispersions has been carried out.

The technology of polymer nanocomposites formation with carbon nanotubes and nonionic surfactants has been developed. The inclusion of disaggregated CNT to polymer composite structure was estimated by scanning electron and atomic force microscope investigation. The results obtained illustrate the mechanism of particle distribution in polymer matrix. Nanocomposite samples (epoxy materials, foamed polyurethane, polyamide papers) were prepared and their mechanical-and-physical properties have been determined. CNTs – surfactants introduction to polymer matrix was shown to improve the complex of nanocomposites properties.

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DEVELOPMENT OF NEW THICKENING ADDITIVES TO OILS ON THE BASIS OF COMPOSITIONALLY HOMOGENEOUS COPOLYMERS

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In modern petrochemistry the polymeric additives are widely used as thickeners for mineral and synthetic oils. Polyalkyl methacrylates and vinyl n-butyl ether homopolymers of various molecular weights are widely used as oil thickeners [1]. However, being effective as thickeners, the above polymers exhibit low resistance to thermal and mechanical degradation. In [2], we suggested using various double copolymers of alkyl methacrylates with vinyl n-butyl (VBE) or vinyl isobutyl ether as thickening additives to mineral and synthetic oils. One of the main characteristics of such copolymers is their resistance to heating and mechanical loads.

This work is aimed to obtaining a new thickener additive on the basis of terpolymers increases the viscosity index of mineral and synthetic base oils. Such a copolymer has been synthesized on the basis of vinyl butyl ether in its copolymerizing with styrene (St) and butyl acrylate (BA).

The synthesis was carried out by dosing the initiator solution in the mixture of the active monomers to the inactive monomer at reflux of it.

Should be noted, that the previously studies of double (St-BA) copolymers were conducted. The research of the copolymer composition were conducted by infrared spectroscopy, the molecular weight characteristics were determined by size exclusion chromatography. It was shown that the copolymer composition at an initial equimolar ratio of the comonomers is not dependent on the dosing procedure, the composition and yield of the copolymer is constant and the ratio of units in the copolymer near to 1:1. However this double copolymer is insoluble in base oils. And for producing a soluble copolymer the third comonomer – VBE was used.

The obtained terpolymer VBE-St-BA was tested as a thickener additive to the base oil AMG-10. It was shown that at the additive concentration up to 5 wt. % a significant increase in viscosity of the oil solution and the viscosity index is observed (table).

Sample	Viscosity, mm^2/s			The relative increase of viscosity at 50 ^{0}c, %	Viscosity index
	at 40 ^{0}C	at 100 ^{0}C	at 50 ^{0}C		
AMG-10	10,7	3,2	8,58	35,78	187
AMG-10 + 5 wt. % VBE-St-BA	15,8	4,4	11,65		208

The resistance of this additive to mechanical degradation was also determined. The research were conducted in according to the GOST 6794-75.

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CREATING NANO STRUCTURED SUBMICRON AND COMPOSITE MATERIALS WITH THE USE OF SUPERCRITICAL FLUID (SCF) ENVIRONMENT

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The unique properties of supercritical fluids (SCF) are widely used in various industries. Supercritical fluids are perfectly suited for use as a solvent, plasticizer or anti-solvent in polymer processing: the modification of polymers, polymer composites, and to obtain a microporous foam particles [1].

One of the promising methods for the preparation of nanostructured composite particles is the method PGSS (Particle from Gas Saturated Solution – particles from gas-saturated solutions). [2] In this method, a supercritical fluid dissolves a impregnation substance and further enriches the molten polymer. After a rapid expansion of the saturated solution through the channel of micron sizes. As a result, supercritical fluid loses its solubility and evaporates into the atmosphere and the molten saturated due to supercooling precipitates as submicron and nanocomposite particles. In this work, an experimental setup for the implementation of PGSS process. As a supercritical fluid used supercritical CO_2. Obtained composite particles ibuprofen/polyethyleneglycol 4000 and methylparaben/polyethyleneglycol 4000. Radiographic phase analysis of these samples showed that the incorporation of individual molecules occurs ibuprofen and methylparaben in single crystals of polyethyleneglycol 4000. Investigated the effect of temperature, pressure and geometry of the channel expansion on the average size of the composite particles. The experimental data may be applied in establishing a new generation of drugs with improved properties.

Revealed that the PGSS process for the average size of the composite particles is significantly affected by the temperature and pressure of the system. By varying the average particle size and porosity varies polymeric carrier. Preparation of materials with predetermined morphology of the porous structure is extremely important and relevant research area of science and technology of polymers. In this paper, as well investigated the influence of thermodynamic parameters of the process on the porosity of polystyrene in supercritical carbon dioxide. To this end , an experimental setup that allows you to conduct research in a wide range of porosity, temperature and pressure. There were changes in the porosity of the polymer with the change of thermodynamic parameters of the process. The data obtained allow to conduct research in the field changes the properties of polymers [3].

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PROBLEMS IN *MISCANTHUS* PULPING

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Miscanthus pulping methods for the purpose of further etherification into ethers are being actively discussed in the foreign literature. As a rule, that is soda pulping with subsequent one-stage bleaching and variants of alkaline delignification. Severe requirements to celluloses meant for the synthesis of esters—cellulose nitrates [1]—dictate the necessity of utilizing the nitric-acid pulping process which allows deriving cellulose rich in α-cellulose from straw raw materials. Complexities in producing cellulose from *Miscanthus* are due to the cellulose content of at most 50% and lignin of 19–21% [2], not high polymerization degree of native cellulose (no more than 1600), and morphological variation of this type of feedstock (stems and leaves) [3]. It has however been found that it is the nitric-acid method which provides quality cellulose from *Miscanthus* in 25% yield on a feedstock basis or 54% on a native cellulose basis. The comparative chemical compositions of Russian *Miscanthus* and nitric-acid cellulose are illustrated in Figure 1, and mass fractions of constituents and polymerization degree of the cellulose are in Table 1.

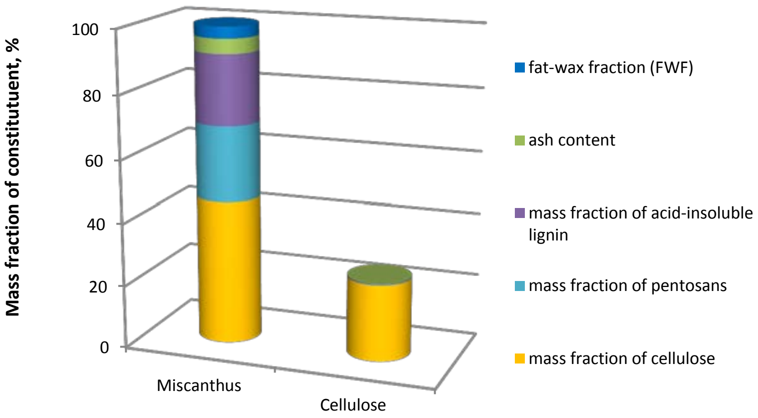

Fig. 1. Chemical compositions of *Miscanthus* and cellulose (%).

Table 1. Mass fractions of constituents and polymerization degree of the cellulose

mass fraction*, %	ash	lignin	α-cellulose	pentosans	PD**
cellulose	0.38	0.91	93.3	0.81	650-970

* on a bone-dry basis, ** polymerization degree

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CHANGES OF PHYSICAL AND MECHANICAL PROPERTIES POLYMERIC COMPOSITIONS IN THE COURSE OF THEIR MICROBIAL DAMAGE

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Recycling plastic waste is a global environmental problem. Most weighty remains disposal carbon-chain polymers (excluding polyethylene), among which a special place is occupied by PVC. One of the most environmentally friendly methods of decomposition of polymers is their biodegradability microscopic fungi. A very effective method of imparting the biological degradability of synthetic polymers is the introduction in the polymeric composition of different fillers, such as the natural polysaccharides (starch, chitosan, cellulose), proteins, etc.

The purpose of our research is investigating physical and mechanical properties of polyvinyl chloride (PVC) and natural polymer compositions in the course of their microbial damage and biodegradation.

Were obtained PVC composition containing from 0.1 part to 1 part by weight polysaccharide based on the weight PVC. Then we investigated the degree of degradation and physical and mechanical properties of PVC based compositions.

The most extensive damage of polymeric material occurs under the action of the associative culture fungi (degree of biological damage is maximum and reaches five points). The most active fungus for these compositions has been identified. This is Aspergillus oryzae. Along with him, active destructor for PVC compositions containing starch is Paecilomyces variotii, for PVC compositions containing chitosan is Aspergillus niger.

Physical and mechanical properties of polyvinyl chloride (PVC) and natural polymer compositions deteriorate after the action of the active microscopic fungus. Breaking stress is reduced by more than forty percent, and the strain reduced by more than twenty percent of the PVC compositions of starch throughout the interval ratio of the components (after the action Paecilomyces variotii). The physical and mechanical properties of PVC with chitosan compositions extensive deteriorate under the action of the associative culture fungi. Breaking stress is reduced by more than twenty percent, and the strain reduced by more than fifty percent.

Thus it can be concluded that the action of different types of microscopic fungus of the different effect on the physical and mechanical properties of polymeric materials. Degree of biological damage of the different types of fungus depends of changes compound of PVC compositions. Findings allow determining of the effective microscopic fungus in developing methods for disposal of PVC wastes.

INVESTIGATION OF MECHANISMS OF THE SULFUR VULCANIZATION PROCESS IN THE PRESENCE OF THE MINERAL ACTIVATOR

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Conventional S-vulcanization of rubbers uses zinc oxide (ZnO) as an activator. ZnO in form of solid particles is typically mixed together with other synthetic rubbers and subjected to heating to accelerate cross-linking. It is of technological interest to replace ZnO with potentially cheaper and environmentally friendlier substances [1]. Although ZnO is not as toxic as other heavy metal oxides, still tire and rubber technical item wastes can contaminate ground waters with zinc ions, which can further react with organic and inorganic compounds giving rise to highly toxic and environmentally dangerous substances. Burning of the wastes is likewise undesirable. Shungite powders have been demonstrated to catalyze S-vulcanization of synthetic, butadiene-styrene based rubbers. Shungite is a rocky mineral and is commercially available. Nevertheless Shungite is composed of mostly carbon and silicon dioxide – environmentally friendly elements. Furthermore Shungite resources are abundant, promising it to be a cheap and environmentally friendly replacement of ZnO for S-vulcanization of rubbers [2].

The shungite powder “Karelit” with a typical diameter of particles in the range of 30 m was provided by “Zhuravskij ochre factory”. Addition of 9 w% of the powder to synthetic rubber accelerated the vulcanization with the mechanical properties of the resulting rubbers being comparable to those of ZnO catalyzed ones. Optical microscopy investigations of vulcanized rubber slices revealed shungite particles 20-50 m in size.

One can’t exclude the presence also others ingredients such as accelerators which contribute to the mechanism of the network formation. Up to our knowledge, however, a number of a group of mercaptobenzothiazole accelerators (2-mercaptobenzothiazole (*MBT)*, 2-benzothiazolyl disulfide (MBTS), N-tertbuty1-2-benzothiazole sulfenamide (TBBS), N-Cyclohexyl-2-Benzothiazole sulfenamide (CBS) etc.) hasn’t been investigated thoroughly before. The chemical structure: bond lengths, angels and especially charges of “S” and “N”, influences not only kinetic parameters of sulfur vulcanization process but also on chemical orientation in close of activators. It has been demonstrated depending on different substituents near the bond “S – N” of accelerators there are changes in structures and views of cure curves. So, results of chemical calculations have good correlation with physical and mechanical properties of rubber blends based on solution and emulsion butadiene-styrene elastomers.

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INTEGRATED WASTE MANAGEMENT BY CHEMICAL PRODUCTION OF COMPOSITE MATERIALS EXTRUSION

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In various industries of Russia now accumulates and is not a huge amount of waste recycled. The bulk of waste – waste chemical production, in particular polymeric materials. Collection and processing of polymeric materials are not properly carried out, all polymer wastes accumulate in landfills and have a long period of decay. In the Orenburg region waste petrochemical industry also constitute a significant segment in the field of waste resulting from the activities of this group of enterprises. Sufficiently strong argument for the speedy and complete as possible recycling is that, as a rule, are highly toxic petrochemical waste and pose a serious threat to the environment [1, 2].

Number of waste by hazard class, used and disposed of businesses owners in %
in the period from 2005 to 2012 [3]

Hazard class Year		II	III	IV	V
2005	-*	-*	-*	-*	-*
2006	25,9	5,8	1,6	4,0	16,5
2007	0,1	4,7	7,0	13,2	8,1
2008	0	0,1	96	71,3	11,1
2009	-*	-*	-*	-*	-*
2010	-*	-*	-*	-*	-*
2011	221,9	0,1	123	-*	-*
2012	-*	-*	-*	-*	-*

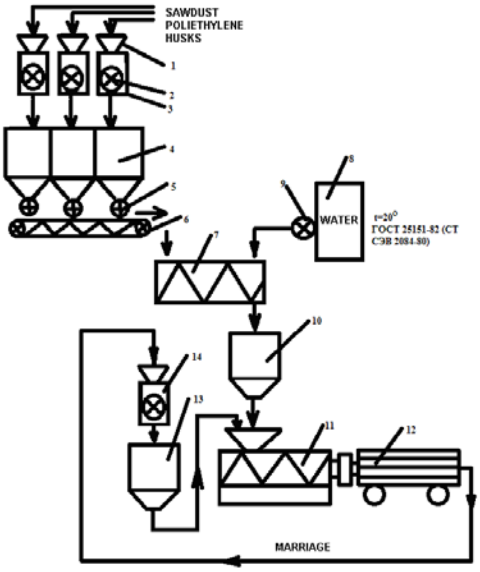
Note: *data in the press are not available or can not be found, for reasons beyond the control of the authors.

Another group consists of food production waste (spent grains, distillery grains, husk), less toxic, but large in terms of education. These wastes or simply merge, due to the inability of the enterprise process it, or used as a fuel (husk), the products of combustion which pollute the environment. If we talk about the timber industry and its waste (chips and sawdust), it is also proper recycling of this waste is not [1–3].

Relevance of integrated waste management by recycling chemical industries in the building materials and related products primarily to the problems of preserving the environment – they are not subject to rotting, corrosion, but also with the problem of resource. Especially promising direction is to obtain utilization of highly plastic, which can be used as building composite materials. It is known that the main aggregates to produce composite materials are screw presses (extruders) [1–3].

To this end, we have developed an integrated approach to waste management of chemical plants, food and wood processing industry by manufacturing composite materials by extrusion.

We have proposed technological scheme for environmentally sound waste material based on chemical, food and wood industries extrusion (Figure 1).



1 – boot device; 2 – sawdust crusher for crushing the LSC-1 (0.2 t / h, 7.5 kW); Crusher for crushing polyethylene MS-500 (180 kg / h 11 kW); crusher for crushing the husks PF -1007 (1000 kg / h, 37 kW); 3 – dispenser; 4 – intermediate hopper; 5 – dispenser; 6 – screw feeder; 7 – mixer; 8 – container; 9 – dispenser; 10 – container otvolazhivaniya; 11 – screw extruder press (180 kg / h, 7.5 kW); 12 – trolley for storage and cooling of finished products; 13 – intermediate vessel; 14 – crusher for crushing marriage RS-500 (180 kg / h, 11 kW).

Figure 1. Flow diagram for production of ecologically safe material
on the basis of chemical waste by extrusion.

The proposed technology can be estimated coefficient of low-waste technology proposed $\text{К}_{\text{МПТ}}$:

$$k_{\text{МПТ}} = (K_{\text{ПЕР.СЫР.}}/K_{\text{ОБЩ.ПОЛ.ПРОД.}})+K_{\text{НЕК.ПОЛ.ПРОД.}},$$

where: $k_{\text{МПТ}}$ – ratio of low-waste technology proposed;

$K_{\text{ПЕР.СЫР.}}$ – amount of feedstock;

$K_{\text{ОБЩ.ПОЛ.ПРОД.}}$ – the total amount of product obtained;

$\text{К}_{\text{НЕК.ПОЛ.ПРОД,}}$ – the total amount of the product obtained from substandard raw materials.

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NEW PERSPECTIVES OF APPLYING OF THE BUTADIENE-STYRENE THERMOPLASTIC ELASTOMERS

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Block copolymer thermoplastic elastomers represent a wide class of materials for universal purpose. However, this materials are largely not been studied, and discoveries of new properties will allow not only expand existing spheres of application, but also get instructions for synthesis new polymers of this class.

Today butadiene-styrene thermoplastic elastomers (BS TPE) are largely apply as elastomer base for solution adhesives used in footwear, furniture and other industries. Block-copolymer structure of BS TPE defines its complex behavior at adhesive film formation and interaction with various modifiers. We have shown that this class of TPE demonstrates amphiphilic adhesive properties. This fact opens yet unexplored capabilities of using BS TPE not only as adhesives but also as antiadhesives together in single product, for example, in medical catheters, stents or endoprostheses.

Our studies show determining influence of the structure of TPE on its adhesive properties. For BS TPE film structure studies bulk and surface methods were used. Bulk methods include transmission infrared spectroscopy, differential scanning calorimetry and physico-mechanical characteristics study. Methods for studying the surface can be attributed the attenuated total reflectance infrared spectroscopy, scanning electron microscopy, contact wetting angle measuring.

BS TPE adhesive characteristics evaluate by the results of delamination adhesive strength experiment at room and increased temperatures, with different substrates. As adhesive TPE solutions were used, with solvents those had different affinity for the TPE. Bacterial precipitation process on TPE films were studied with dependence on polymer bulk and surface structure.

BS TPE structure varied by both polymer selection and its properties changing by means of film formation from different solvents and by pre-adhesion thermoactivation time varying. Samples composition and its obtaining conditions influence were also examined: on surface layer composition (including relation to the bulk) and surface characteristics and adhesive properties towards different substrates.

Results obtained indicate substantial effect of both initial and formed by polymer processing structure on BS TPE adhesive properties. There was shown that surface properties have defining relation for adhesive characteristics. Certain TPE macromolecules output to the surface depends on both TPE chemical structure and sample preparation conditions. Therefore, by changing adhesive layer obtaining conditions one can attach both adhesive and antiadhesive properties to the surface. Antiadhesive properties are crucial to prevent bacterial precipitation on TPE surface. It is shown that in this case surface properties are also defining.

Topicality of TPEs amphiphilic properties studying is associated with the need to solve the problem which is extremely important to human life – the problem of bacterial film formation and growth on material surfaces. Its solution is related with extension of using these materials in various products that contact with microorganisms – from products working in natural water and soil to medical products working in non-sterile medium.

CHLOROCONTAINED EPOXYACRYLATES: SYNTHESIS AND MODIFICATION PROPERTIES

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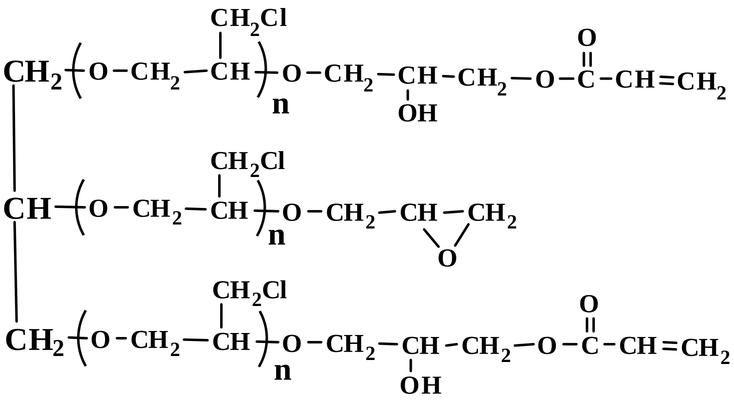
The epoxyacryl compounds, which obtained by interaction of the epoxycontained oligomers of acrylic acid, are widely used as modifiers for epoxy resins.

Use them as the reactive modifiers allow obtaining the polymeric materials with the low residual voltage, high elasticity, high adhesive and impact resistance.

(Most often the compositions, which contained as modifier the oligoester acrylates, during the structuring chemically not bonded with molecules of the epoxy resin).

The present work is devoted to the synthesis and study of modifying properties of chlorocontained epoxyacrylate oligoesters on the base of polyoxychloropropylenetriepoxy compound, which synthesized by the method described in [1–2].

The esterification of chlorocontained triglycidil ether of acrylic acid was carried out in toluene in presence of pyridine (0,1 mol % of te total quality of reagents). The reaction was controlled by the acid-base titration (0,1 N in aqueous solution of KOH, the indicator is bromothymol blue).



The synthesized epoxyacrylate was tested as modifier-flame retardant of resin ED-20.

The polyethylenepolyamines (PEPA) in amount of 18 m.p. and bromendic anhydride in amount of 70 m.p. were used as the curing agent (hardener).

The degree of hardener of compositions was evaluated by acetone extraction of the crushed samples in Soxhlet apparatus during 6-8 hours.

In the tested samples the degree of hardener is not less than 96-98%. For comparison under identical conditions were prepared the compositions of ED-20/PEPA.

It has been shown that the physical-mechanical properties of epoxy compositions with a modifier considerably higher than those for the compositions of ED 20/hardener as in the case of the polyamine, and in the case of the anhydride hardeners.

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SYNTHESIS OF ORGANOSILOXANE COATINGS FOR SURFACE MODIFICATION OF TEXTILE MATERIALS

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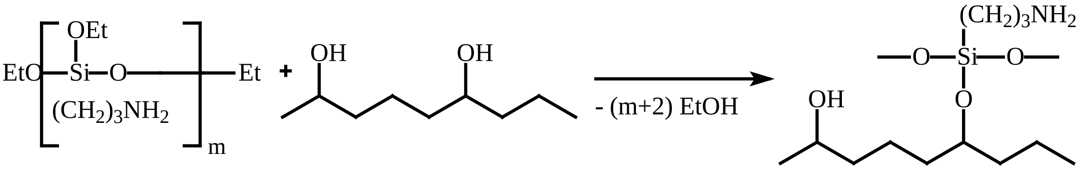
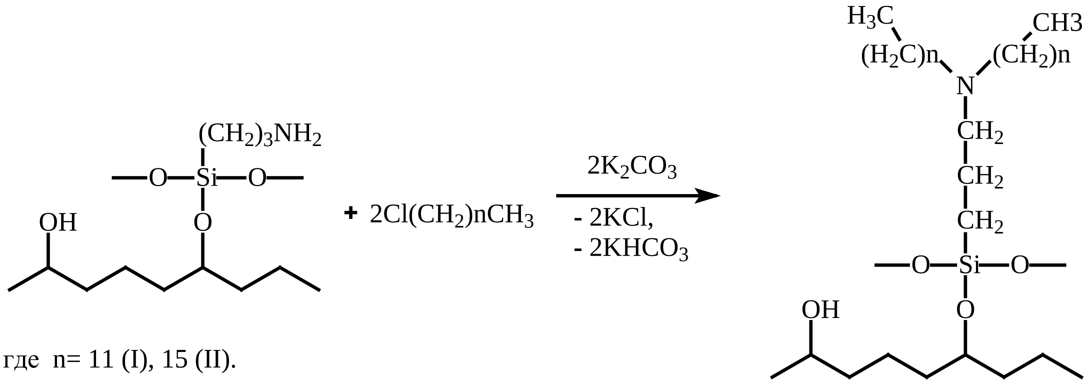
A method for chemical modification of the surface of fibers and films by layered molecular assembly of a new hydrophobic grafted surface organosiloxane coating is developed, according to which nanolayers of aminopropyl organosiloxane coating are the covalently attached to the surface of the material followed with treatment by alkyl chloride (C12-C16), that lead to the grafting of monomolecular finish layer with high dialkyiliminopropyl groups.



где m= 5, 10, 15, 20; Et= C_2H_5.



где n= 11 (I), 15 (II).

I, II

It was established that the affectivity of the hydrophobic properties of the coating (I) and (II) depends on the structure and quantity dialkyiliminopropyl groups on the surface. Thus, the contact angle for the cotton fabric, surface of which contains 0.3 wt % for coating (I), is 128°, and for coating (II) – 130°. For cotton/ester fabric – 140 and 148°, respectively , and for viscose polyester – 138 and 142°, respectively. Waterproof of coated with samples (I) and (II) fabric is 3.4 – 18.3 kPa higher than the waterproof fabric coated with traditional water repellent GKZH-94, and the water absorption is 2 times lower. The contact angle of tissues modified coating (I) and (II) 129–149° achieves that by 31–51° higher than GKZH-94-modified tissue samples.

Thus, we have developed a new graft surface organosiloxane coating dodecylalkensulfide and high dialkyiliminopropyl groups. These new approaches of stepwise consolidation of these coatings on the surface of the fibrous and film materials are very promising for use in the chemical technology of finishing of textile polymeric materials.

ALIPHATIC POLYESTER-BASED BIODEGRADABLE SURFACTANTS FOR ENCAPSULATION TECHNIQUES

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Aliphatic polyesters based on hydroxyacids – lactic, glycolic, etc. are widely used in medicine due to their biocompatibility and ability to decompose into non-toxic and easily excreted compounds. During the last decade attention of researches is devoted to amphiphilic aliphatic polyesters due to their biocompatibility and good surface properties. In course of degradation of such polymers mainly natural metabolites are formed, that makes their use in medicine and biotechnology are particularly attractive. Such polymers, having hydrophobic polymer blocks formed by hydroxyacids, and hydrophilic ones by polyethylene oxide and polyglycerols, may present new biocompatible and biodegradable surface- active compounds that are able to withdrawn from the body rapidly and completely.

In this work, a series of new block copolymers based on hydroxy acids was synthesized and studied, as well were defined their physico -chemical and surface properties. All synthesized amphiphilic block copolymers possess pronounced surfactant properties, depending on the ratio of the hydrophilic and lipophilic moieties the macromolecule, as well as the structure of the copolymer. We present the sucessful usage of synthesized aliphatic polyester-based biodegradable copolymers as surfactants in the preparation of microemulsions, microcapsules and microparticles. It was established that the droplet size for emulsions stabilized by branched copolymers grew more slowly than for emulsions, stabilized by the linear ones. Microcapsules, formed using the branched copolymers as surfactants, show higher encapsulation efficiency and smother particle surfaces compared to ones, formed using the linear copolymers.

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INVESTIGATION OF CREEP HDPE AT TEMPERATURES CLOSE TO MELTING

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HDPE investigated creep at 100°C with stepwise loading mode . Developed a technique to study the creep HDPE transition temperature creep region. Found step change in the limit to the yield point .

An increasing number of PE grades. One promising PE grades, a PE-100, which is compared with a PE-63 5.3% suspension of the monomer and another bimodal MWD. In this paper, we study the deformation properties of this material.

One of the methods for studying the deformation properties of the polymers is to build

creep curve . It gives us limited information on the elastic and viscous deformation of the sample . In our work, has been investigated in the creep mode, the step of loading onto the unit , which is filled with a heated silicone oil bath (Figure 1) In which a polymer sample is immersed and uniformly heated therein to 100°C, is the temperature at which the mobility partly crystalline structures.

Next, we are suspending cargo and wake behind the sample, the whole essence of the method is that we are adding loads when we see that the sample is sufficiently long period of time is not deformed . And so prior to necking .

From the data obtaine , we can construct a graph of deformation of the sample over time. (Figure 2).

This curve corresponds to a certain speed deformation of the crystal field. When the area is completely deformed, the deformation stops. Upon further loading the sample probably begin to deform more ordered crystalline regions and appears the next step on the curve. We come again to the limiting value of the deformation and so on up to necking. When the neck is formed, then there was a strain of crystalline regions. Thus curve is presented as an expression of mechanical spectroscopy to the crystal structure of the polymer.

It seems to us that this is a new method of investigation and the crystal structure of polymers and its ability to deform. We constructed a curve , if plotted in the coordinates of the stress- strain curve corresponds to the initial portion of the load and elongation as follows. (Figure 3)

The next step should be to find methods for studying the structure of the polymer. You might think about the method of birefringence given by which also had to be changed in steps.

Found creep stepwise change which may be regarded as mechanical spectroscopy crystalline structures.

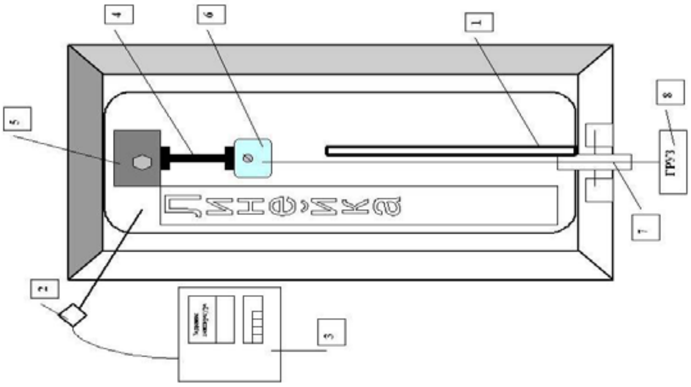

Fig. 1. Instrument for measuring the creep at variable voltage (1 - bath with electric, 2 - thermocouple, 3 - temperature controller, 4 - sample, 5 - stationary clamp, 6 - movable clamp, 7 - unit, 8 - load).

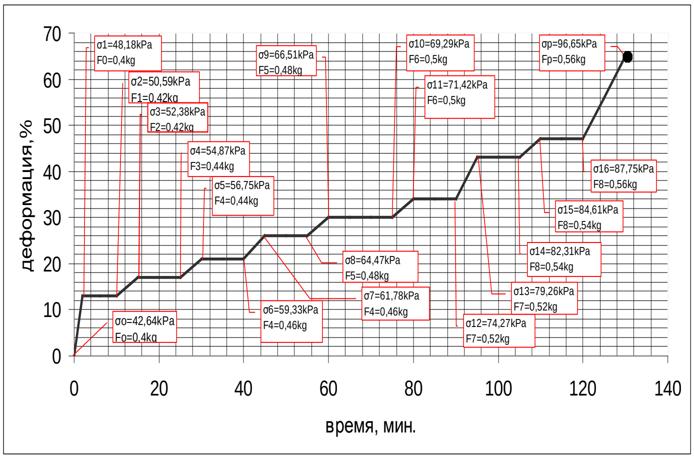

Fig. 2. Creep PE-100 at 100°C and a variable load.

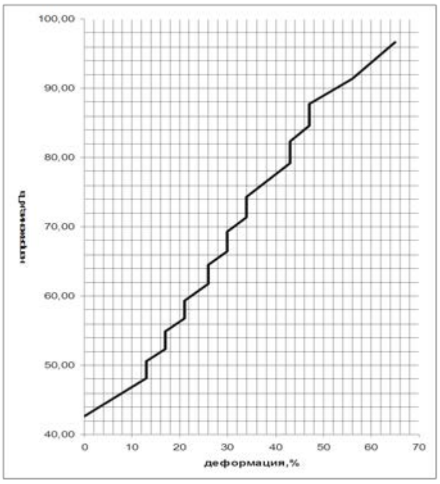

Fig. 3. Dependence of the stress-strain PE-100 at 100°C at variable load.

PREPARATION OF HIGHLY SWELLABLE BIOLOGICALLY ACTIVE FILMS BASED ON CHITOSAN MODIFIED BY POLYPHOSPHATES

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Natural amino-containing polymers are widely used in the creation of materials for biomedical application: modern dosage forms, biologically active suture filaments and wound dressings, biosorbents etc. A promising natural polymer to create hydrogel materials for medicine is chitosan [1]. Depending on the application, chitosan-based materials should have a certain complex of predetermined properties. The use of crosslinking reagents of different types allows to control properties of obtained materials, and to extend its range of potential applications. The presence of positively charged groups in chitosan macromolecule makes it possible to carry out crosslinking of the polymer by polyanions, especially by polyphosphates, due to electrostatic interactions [2].

The aim of the study was to obtain film materials for biomedical application with predetermined properties based on chitosan using ionic crosslinkers. Sodium tripolyphosphate and potassium pyrophosphate were used as ionic cross-linking reagents. In the study films were obtained from 1–4% (w/v) chitosan solutions in dilute acetic acid, modified by polyphosphates using two methods: surface treatment by polyphosphates and incorporation of crosslinkers into spinning solution. The calculated and experimental dependences of the number of negatively charged groups in the tripolyphosphate and pyrophosphate molecules and protonation degree of the chitosan amino groups on the pH allowed to define optimum conditions for ionic crosslinking. Incorporation of the sodium tripolyphosphate in the spinning solution with a concentration higher than 1% leads to rapid coagulation. The use of chitosan solution with a concentration 1% (w/v) allowed to incorporate tripolyphosphate into the spinning solution and to obtain by solvent evaporation water-insoluble film with swelling degree up to 3000%. Replacement of tripolyphosphate on pyrophosphate, containing 4 acid groups per 1 crosslinker molecule, resulted to obtaining of film with greater swelling capacity (up to 4000%), and in this case it was possible to incorporate the crosslinking reagent to the spinning solution with chitosan concentration 4%.

Anesthetic lidocaine and antimicrobial agent miramistin, which effectively prevents wounds and burns infection and activates regeneration, were used as biologically active compounds to impart an antimicrobial activity and analgesic action to chitosan-based films. The drug release rate is one of the most important parameters of drug-loaded materials that define its pharmacokinetic properties. Drug release increased from 30 minutes up to 24 hours, depending on the film thickness and processing time by tripolyphosphate. The antimicrobial activity of obtained films was investigated in relation to a number of pathogenic germs. The results showed that their activity was maintained at a high level during 2 hours of holding in physiological solution to all investigated strains: *Staphylococcus aureus, Eschrichia coli* and *Pseudomonus aeruginosa*.

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PROPERTIES OF ELASTOMERIC COMPOSITIONS, CONTAINING COMPOSITE VULCANIZATION ACTIVATOR

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An obligatory component of any sulfuric vulcanizing system is accelerators activators which allow getting rubbers with a higher complex of physical mechanical properties. Vulcanization activators improve technological and performance properties of rubbers. The nature of the effect of activators significantly depends on the type of a rubber phase of the rubber mix, the applied accelerators of curing and fillers. The most widely applied activators are zinc oxide and stearin acid. The content of zinc oxide in rubber mix usually composes 3–5 phr. and of stearic acid – 1-2 phr.

However, in view of zinc oxide deficiency and ecological aspects of its influence on the environment development of compoundings of the elastomeric compositions containing the lowered dosage of the main vulcanization activator is topical. In connection with this the composite substances containing at the same time a combination of primary and secondary activator are of great interest. The aim of the research was to determine the effect of Vulkativ composite activator (produced by JSC Sovtekh, Voronezh) on properties of elastomeric compositions after partial replacement of zinc oxide and stearin acid with Vulkativ.

The Objects of the research were tyre rubber mixes based on natural rubber (NR) and combinations NK+BR (stereospecific butadiene rubbers), NK+BR+IR (isoprene rubber), containing combinations of activators of curing in various ratios. Vulkativ composite activator is a composition containing oxide of zinc, salt of phytogenous fatty acids, saturated fatty acids and target additives. Mooney Viscosity test is a widespread method in international practice, which allows defining both quality of raw rubber, and prediction of technical characteristics of elastomeric compositions. It has been determined that Mooney viscosity of the rubber mixes containing a combination zinc oxide: Vulkativ in ratios 75:25 and 50:50 changes from 0,5 to 2,5 Mooney units. Since the composite activator contains saturated fatty acids, partial replacement of the main activator was observed and the content of stearin acid was reduced. With the increase of quantity of the new activator in rubber mix Mooney viscosity decreased by 1,2–1,4 times. The change of viscosity is probably caused by additional plasticizing effect of salts of fatty acids. Vulcanization is the final process of rubber items production. The analysis of the curves of vulcanization process showed that for all the studied elastomeric compositions periods of optimum time of curing differ by 2–6%. It should be noted that in case of increase of the new composite activator content (in case of partial replacement of stearin acid with it) optimum time of curing increases by 11–21%. Determination of the stress-strain properties of rubbers showed that the use of Vulkativ leads to improved elasticity, except for rubbers based on NK+BR. Partial replacement of zinc oxide and stearin acid with the composite activator leads to reduction of strength properties of vulcanizates. It is probably caused by changing of cross-link density and also the nature of the forming bonds.

Thus, the results of the researches showed that in tyre rubber mixes it is possible to replace an expensive and scarce component of zinc oxide with the composite activator of vulcanization Vulkativ in quantity to 50%. It doesn't lead to considerable changes of technological properties of rubber mixes and technical performance properties.

STUDY OF THE CONDUCTIVITY OF POLYMER NANOCOMPOSITES FILMS BASED ON POLY-*para*-XYLYLENE

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The field of nanotechnology is one of the most popular areas for current research in all technical disciplines. This definitely includes nanostructural composite materials investigation as electrical, optical, mechanical properties of these materials are changed at introduction of a metal (semiconductor) phase in a polymeric matrix. At a concentration of nanoparticles close to the percolation threshold nanocomposites exhibit unusual in comparison with volume materials electrophysical properties, which are the subject of increased attention of the researchers working in the field of chemistry and physics of low-dimensional systems.

This work reports a dark conductivity dependence at room temperature in poly-para-xylylene – nanoparticles composite films with different concentration of nanoparticles (C = 2–100 vol. %). Nanoparticles of Fe, Co, Ni, Sn и PbS were used.

Nanocomposite films are synthesized by vacuum co-condensation of the metal (semiconductor) and a monomer (para-xylylene) vapours [1] on a cooled (77 K) substrate from sital with superficial electrodes like "comb", 20 teeth from each side, distance between teeth of 70 microns. Thickness of the films is of ~0.5mcm. Electric measurements were carried out by a two-probe method in the Leybold cryostat with the help of the automated laboratory facility of a direct current on the basis of the electrometers SMU 237 Keithley and TR8652 Advantest.

It was found out the resistance R(C) decrease for all nanocomposites with the increase of nanoparticles concentration up to C = 8÷10 vol. % for all nanocomposites. The maximum reduction is ~ 10–12 orders for composites with Fe and Sn nanoparticles.

The resistance of the films of the nanoparticles (C = 100 vol. %) decreases by ~ 10 orders in line PbS>Co>Sn>Ni>Fe and for the films of nanoparticles of Fe, Ni and PbS (C = 100 vol. %) is of the same order, as the resistance of composites with the concentration of nanoparticles of C = 10 vol. %, and for Sn and Co – is more in 7 and 4 orders, respectively.

A dark conductivity dependence on temperature (10–300K) in poly-para-xylylene –Fe nanocomposite films with different concentration of Fe nanoparticles (C_{Fe} = 2–100 vol. %) was also studied. It was found out that the conductivity of the films with C_{Fe} = 2–12 vol. % monotonously decreases at the temperature range from 300 K to 15 K. For the films with C_{Fe}<10 vol. % the dependence of σ (T) in the temperature range of 300 – 150 K is well approximated by the model of Mott hopping conductivity with a variable length of a jump. For the films with C_{Fe} =14 vol. % in the range T = 300 ÷ 230 K there is a monotonous decrease and at T < 230 K there is an increase of the conductivity (the “metal” nature of the temperature dependence of σ (T) takes place). In the pure Fe films (C_{Fe} = 100 vol. %) σ (T) changes on the metal type.

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A NEW STRATEGY OF SYNTHESIS OF POLYSILOXANES BY CASCADE HYDROLYTIC POLYCONDENSATION ORGANOCHLOROSILANES

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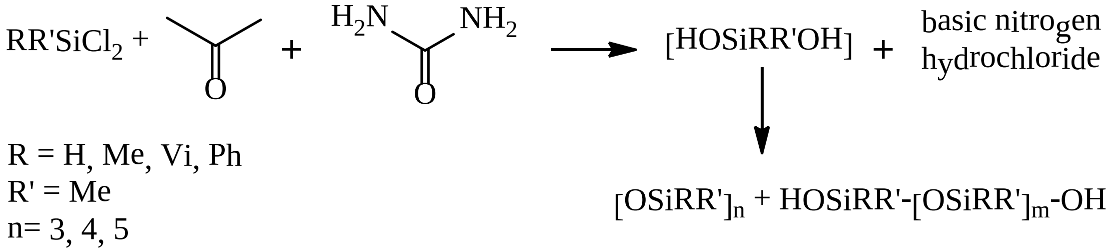
The method for preparation polyorganosiloxane by hydrolytic polycondensation of organodichlorosilanes (DCHS) in the system DCHS – carbamide (CA) – ketones have investigated. Synthesis takes place in anhydrous inert solvents, in which generation of water is provided through condensation ketone with carbamide. Water formed during the condensation is spent on hydrolysis of organodichlorosilane. The general scheme of the process:



Ketones and carbamide (in the absence organochlorosilanes) not interact at room temperature. However, in the presence of chlorosilane and slight heating condensation start at an appreciable velocity with heat. “Coupled” reactions – condensation ketone with carbamide and hydrolysis organochlorosilane – proceeds with quantitative yields. As a result, oligoorganosiloxanes (mainly cyclic structure) and a basic nitrogen hydrochloride are formed.

An influence both of ratio values of reactants (DCHS: CA: ketone) and the nature of solvents used on yields, composition and structure of resulting oligoorganosiloxanes was studed.

It is found that at non-polar solvents under complete binding of evolving hydrogen chloride output jf strained cyclotrisiloxanes reaches $\leq$ 65%.

OXIDATION RESISTANCE COMPOSITIONS BASED ON 1,2-POLY-BUTADIENE CONTAINING NANOSCALE TITANIUM DIOXIDE OF DIFFERENT MODIFICATIONS

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One promising directions is the creation of polymer nanocomposites, which are formed by mixing polymers and nano-fillers of different nature. At the moment of greatest interest nanoscale modification of titanium dioxide (NDT). Their uniqueness is caused by formation of surface hydroxyl groups with a high reaction activity, which lead to changes in the properties of substances, such as solubility, transparency, color, conductivity, melting point, phase transition temperature and the other, as well as the appearance of new properties: photocatalytic and sorption [1].

Most polymer nanocomposites with processing, storage and operation are oxidized, which leads to deterioration of its properties. Most sensitive to oxygen polydiene rubbers.

Object of research in this work is 1,2-polybutadiene brand SKD-CP containing as functional additives NDT different compositions, specific surface area, particle size and the coherent scattering region.

Control over the process of oxidation was carried out by measuring the amount of oxygen absorbed by the polymer. For registration of the oxygen absorption using the vacuum system, consisting of a reactor vessel and related manometer [2]. Oxidation was carried out at 160 and 180^{o}C. Also the performed EPR-spectroscopy of samples to establish the influence of NDT on the mobility of macromolecular chains.

The test results of samples

Samples	The oxidation rate W_{O2}, mole/kg*s		The correlation time *10^{-10}, s
	160 ^{0}C	180 ^{0}C	
1,2-PB+VG	5*10^{-5}	11,1*10^{-5}	6,5
1,2-PB+VG+TiO_2 sv 60	2,2*10^{-5}	8,3*10^{-5}	6,5
1,2-PB+VG+TiO_2 sv 66	2,2*10^{-5}	8,3*10^{-5}	6,5
1,2-PB+VG+TiO_2 sv 68	2,2*10^{-5}	8,3*10^{-5}	6
1,2-PB+VG+TiO_2 sv 70	2,2*10^{-5}	8,3*10^{-5}	6
1,2-PB+VG+TiO_2 sv 71	2,2*10^{-5}	8,3*10^{-5}	6

As a result of the spent researches observe that NDT has no effect on the mobility of macromolecules in the structure of the composition, as well as an insignificant effect on the rate of oxidation.

Thus, introduction of NDT, regardless of particle size and specific surface area does not affect the oxidation behavior.

This work was financially supported by the Russian Foundation for Basic Research (project No. 14-03-00917).

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COMPOSITIONS ON THE BASIS OF ALICYCLIC POLYIMIDE WITH POLYURETHANE

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Nowadays wide studies have been conducted to develop new polymeric materials representing individual high-molecular compounds and compounds of several substances with not only additive, but also new synergetic properties. Integration of various additives is known to modify properties of studied polymers, obtaining materials with certain performances, for example, improved tensile strength, electric conductivity, plasticity or high rigidity, chemical resistance, and etc. Generally these additives are added in small amount, however they provide a significant effect. Published works are mainly related to polyimides of aromatic structure. At the same time alicyclic (semiaromatic) polyimides, also interesting for different technique fields and particularly obtained on the basis of dianhydrides of tricyclodecentetracarbon acids and different diamines, can be modified by different low- and high-molecular compounds, obtaining new polymeric systems with improved physical and mechanical characteristics.

We have shown before that polyimides with tricyclic decenoic fragments in the main chain can be modified by polyurethanes on the basis of *n*-toluenediisocyanate and di(ethylene glycol) with MM 400; as a result higher strength and elasticity films have been obtained comparing to initial polyimide. However, detailed investigation of these film properties revealed that film tensile strength can be significantly improved by other, more complex polyurethanes. The goal of this study is to research influence of polyurethane on the basis of 4.4'-methylene-bis-(phenylisocyanate) and [poly(ethylene glycol) – propylene glycol – poly(ethylene glycol)] oligomer on the formation process and on the main properties of new polymeric systems where the main component is alicyclic polyimide based on dianhydride of tetracarbon acid and oxydianiline. Polyurethane based on PEG-PPG-PEG oligomer with MM 2900 and 1100 was used for the further investigation.

Electric parameters in the presence of PU irrespective of initial oligomer molecular weight are slightly changed: a tangent of angle of dielectric losses in total range of polyurethane concentration is 0,004–0,006, dielectric permeability is 2,0–2,6; breakdown voltage is 150–180 kV/M, values of specific volume resistance (2-4)•$10^{(14\text{-}15)}$ Ohm M, these values for non-modified polyimides are in range (2-4) $10^{(15\text{-}16)}$ Ohm•M. It can be noted that electric characteristics are at the initial polyimide level, used polyurethane concentration does not effect on the dielectric parameters.

The thermal characteristics are higher as well: T_{ds} of PU compounds for 2,0% of weight is 275°C; 10% of weight are lost at 360°C; 25 and 50% weight loss at 425 and 550°C respectively; for PI+PU system based on n-toluenediisocyanate and di(ethylene glycol) similar weight loss is fixed at 255, 346, 425 and 420°C, in the first case the composition decomposes at higher temperatures, by 15–25°C.

Characteristic performances of alicyclic polyimide modified by polyurethanes based on 4,4'-methylene-bis-(phenylisocyanate) and [poly(ethylene glycol) – propylene glycol – poly(ethylene glycol)] oligomer of 1100 and 2900 molecular weight and by polyanilines have been studied. The optimal quantity of modifying compounds has been found.

SYNTHESIS OF COPOLYIMIDES CONTAINING ALIPHATIC POLYETHER FRAGMENTS

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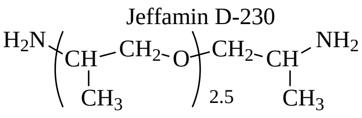
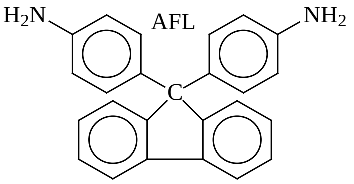
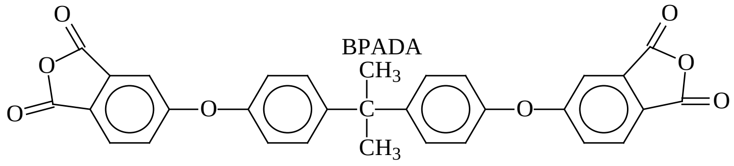
In a course of the high temperature synthesis of polyimides and copolyimides (CPIs) from tetracarboxylic acids dianhydrides and highly basic diamines, technological difficulties appear often because of the by-reaction of amino groups with carboxylic groups of transient amic acid fragments. Such an interaction may lead to gel formation in a system. This drawback can be avoided by the use of molten benzoic acid (BA) as reaction medium instead of nitrobenzene or m-cresol usually used. The BA molecules compete with carboxylic groups of amic acid fragments for amino groups and thus prevent gel formation. Besides, effective reactivity of amino group is mediated by BA as reversible binding agent, in the same time, catalyst of acylation stage. Recently, it was established that change in the intermonomer loading order can be used to control CPI chain microstructure: the one-shot loading leads to random CPI whereas slow addition of intermonomer to the comonomers mixure leads to multiblock CPI. In this work, we successfully used said approach for obtaining new CPIs series. Eethylene oxide-co-propylene oxide oligomer with two amino end groups (Jeffamine D-230) and 9,9-bis(4-aminophenyl)fluorine (AFL) were used as comonomers. 2,2-bis-[(3,4-dicarboxyphenoxy)-phenyl]-propane (BPADA) was used as intermonomer.







Samples of CPIs synthesized were investigated by DSC. CPI sample obtained in a process with the one-shot loading (presumably random chain microstructure) displays only one heat capacity jump at 150°C related to the glass transition Tg, which value is in between the Tg values of corresponding homo polymers (T_g = 75 and 300°C). The samples obtained with slow intermonomer loading to the comonomers mixture having presumably multiblock chain microstructure display two heat capacity jumps related to the two phase morphology. All the CPIs samples obtained are soluble in $CHCl_3$ and possess thermoplastic behavior. Strong transparent films were cast from $CHCl_3$. The CPIs synthesized are of interest as materials for gas separation membranes.

Work was supported by RFBR, grant No. 03-13-00915

SELECTIVE DEPOSITION OF SILVER NANOPARTICLES ON THE SURFACE OF HONEYCOMB-PATTERNED CARBOXYLATED NITROCELLULOSE FILM

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Composite materials in which metal nanoparticles coated the surface of microstructured honeycomb film are of interest in photonics and electronics and can be used, for example, as substrates for Raman scattering spectra registration [1, 2]. The aim of this work was the formation of microstructured ordered honeycomb films coated with silver nanoparticles. Honeycomb-patterned polymer films were prepared by water-assisted method from carboxylated nitrocelluse (CNC) solution in *i*-amyl acetate/*n*-buthanol [3]. Formed films were modified by silver nanoparticles using electroless plating. Silver cations have been adsorbed on the honeycomb film followed by theirs reduction to metal nanoparticles by sodium tetraborate.

The optimal conditions which allow forming silver layer only onto the surface of polymer honeycomb films were determined. It was established that the key factor which affects the selectivity of Ag^0 deposition is the duration of CNC honeycomb film treatment by $AgNO_3$ solution. So, modified with silver nanoparticles ordered honeycomb films can be produced if initial polymer films are treated with $AgNO_3$ solution for 2–5 minutes (figure). Increase in time of film treatment by $AgNO_3$ solution up to 10–30 minutes leads to precipitation of Ag nanoparticles both on the film surface and inside cells.The varying of the concentration of silver nitrate solution (from 3 to 10 mg/ml), the duration of film treatment by reducing agent (from 5 to 30 min) and its concentration (from 0.1 to 0.5 mg/ml) influence only on the density of silver nanoparticles on the surface of honeycomb CNC films.

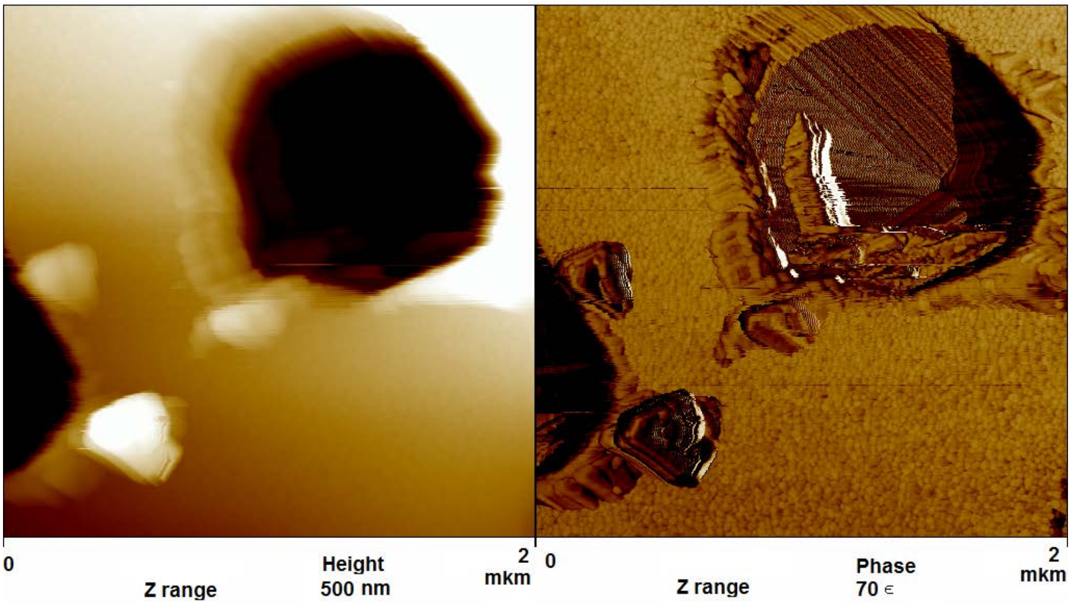

Fig. AFM-image of honeycomb film from carboxylated nitrocellulose modified by Ag nanoparticles.

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MODIFICATION OF POLYESTER TEXTILE MATERIALS BY APPLICATION OF WATER REPELLENT COATING IN SUPERCRITICAL CARBON DIOXIDE

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There is an increasing demand for water-resistant textiles on the textile materials market, so that the problem of obtaining household and industrial fabrics with high hydrophoby is pressing. The primary of objective of textile modification is to impart water repellent properties (hydrophobic finishing) to textile materials, while maintaining the air (water vapor) permeability, which effect is achieved via formation of a coating characterized by low surface tension energy. The main indicator of hydrophobicity of materials is the contact (wetting) angle Θ which exceeds 90° in the case of hydrophobic materials. The focus of special researchers' attention is on highly hydrophobic materials (ultrahydrophobic, $\Theta > 120°$, and superhydrophobic, $\Theta > 150°$). The surface energy of fabrics can be reduced by treating with hydrophobizing agents among which fluorinated hydrocarbons exhibit the highest efficiency. These agents are deposited onto fibrous materials from emulsions or suspensions. However, the resultant coatings get contaminated with trace amounts of emulsifiers and, moreover, exhibit insufficient stability under conditions of use.

We used the way of dissolution of the low-molecular-weight fraction of ultradispersed polytetrafluoroethylene powder in supercritical carbon dioxide. Due to formation of coatings from solutions rather than from emulsions or suspensions, these technologies avoid the above-mentioned shortcomings.

Here, we report on a study concerned with modification of polyester fabric. Polyester fiber is known to be hydrophobic, but fabrics manufactured thereof have an intricate capillary-porous structure and do not possess hydrophobic properties: fluid droplets getting thereon are instantly absorbed by inter-fiber spaces. Hence, it seems appropriate that a woven material, rather than an individual fiber, be subjected to modification treatment.

As hydrophobizing agent served a Forum trademark ultradispersed polytetrafluoroethylene powder developed by the Institute of Chemistry, Far-Eastern Branch, Russian Academy of Sciences. The preparation procedure for this product is based on thermal gas-dynamic decomposition of polytetrafluoroethylene waste accumulated at industrial facilities. This material consists of low- and highmolecular weight fractions, of which the former comprises mainly 13–16 units, and specifically this fraction dissolves in supercritical carbon dioxide.

We showed that treatment of the polyester fabric with a solution of ultradispersed polytetrafluoroethylene in supercritical carbon dioxide results in formation on the surface of the fibers constituting the fabric of an ultrathin low surface energy coating possessing an ordered structure and demonstrating high stability under conditions of use. The fabric hydrophobized with Forum exhibit improved performance characteristics. The treated polyester fabric acquires ultrahydrophobicity and a record-low percentage of water absorption. The water vapor permeability of the fabric increases, while its air permeability slightly decreases.

CURING KINETICS OF EPOXY COMPOSITES MODIFIED BY POLYANILINE

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It is known that polyaniline (PANi) is a unique polymer having a plurality of different shapes which are capable of reversibly transform into one another under the influence of external factors (Figure 1). This opens up opportunities for the use of PANi as a catalyst for certain types of reactions, such as hydrolysis of esters of glycerol and others.

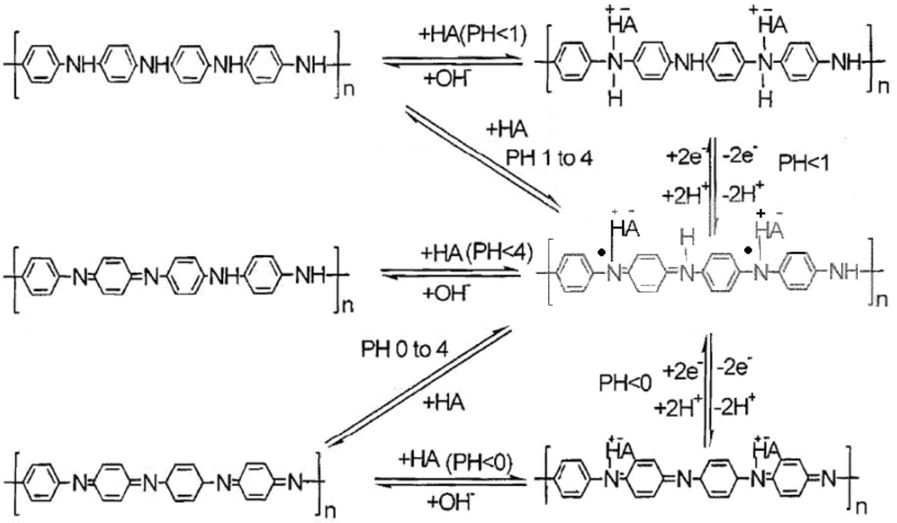

Figure 1. Scheme transition forms of polyaniline under the influence of various factors.

Given the presence of redox properties of PANi reduce reasonable to assume that in the process of aging may change the structure builder. The consequence may be a radical change in the properties generated using the modified PANI amine cross linking agent, epoxy polymer materials. This way, of great interest to study the stability of the modified amine cross linking agent over time. In addition, it is necessary to evaluate the impact of transformation occurring as a builder of PANi on the curing of epoxy oligomers.

As objects of study used epoxy oligomer epoxy equivalent of 205 g/eq . As hardener used amine hardener H- equivalent of 29 g/eq. As a builder and used undoped emeraldine and pernigraniline form of PANI. Absorption spectra of PANI-modified amine cross linking agent (AH) were prepared using a spectrophotometer Specord M-40. Epoxy group content was determined by infrared spectroscopy. Kinetics of the curing of epoxy composites was investigated using a sol - gel analysis of a calorimetric method, and IR spectroscopy.

It is shown that in the process of storing the modified AH converting the emeraldine form PANi in pernigraniline, as evidenced by the shift of the peak on the absorption spectrum. Using sol - gel analysis and calorimetric method to investigate the process of curing epoxy oligomer in the presence of emeraldine and pernigraniline forms PANi. It was determined that the modified AH with PANi content to 0.57 wt%. do not lead to slower cure, and consequently the complex operational properties of epoxy resin coatings formed on their basis. Found that the use of a modified form pernigraniline AH from PANi high content leads to inhibition of the curing process of the epoxy composition. It is shown that the introduction of a reducing agent leads to pernigraniline reconverted to form PANi emeraldine.

MODERN TRENDS IN A FIELD OF OBTAINING BLOCK COPOLYMERS AND COPOLYMERS WITH GIVEN MOIETIES DISTRIBUTIONS

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Short review concerning the state of the art in a field of synthesis, structure investigations and application areas of copolymers with given moieties distribution in chain and block copolymers (BCP). The first part of the lecture is devoted to consideration of polycondensation-type copolymers with given moieties distribution obtained from symmetrical and non-symmetrical comonomers (random, multiblock-,alternating, “head-to-head”). In the second part of the lecture, experimental methods for obtaining block copolymers are considered including controlled radical polymerization, coupling of reactive oligomers, combined methods, trans-reactions, mechanochemical synthesis, and so on. Parameters are considered which are used for BCP characterization and classification (chemical composition, the number of blocks in chain, the number of block types in chain and so on). Factors influencing on the phase morphology are considered as well as instrumental methods for its investigation. Some properties of BCP and perspective application areas are discussed including preparation of frost-resistant plastics, gas separation and ion-conducting membranes, materials for electronic industry.

CREATING THE ADHESIVES WITH ENHANCED CHARACTERISTICS ON THE BASE OF BUTADIENE-STYRENE THERMOPLASTIC ELASTOMERS

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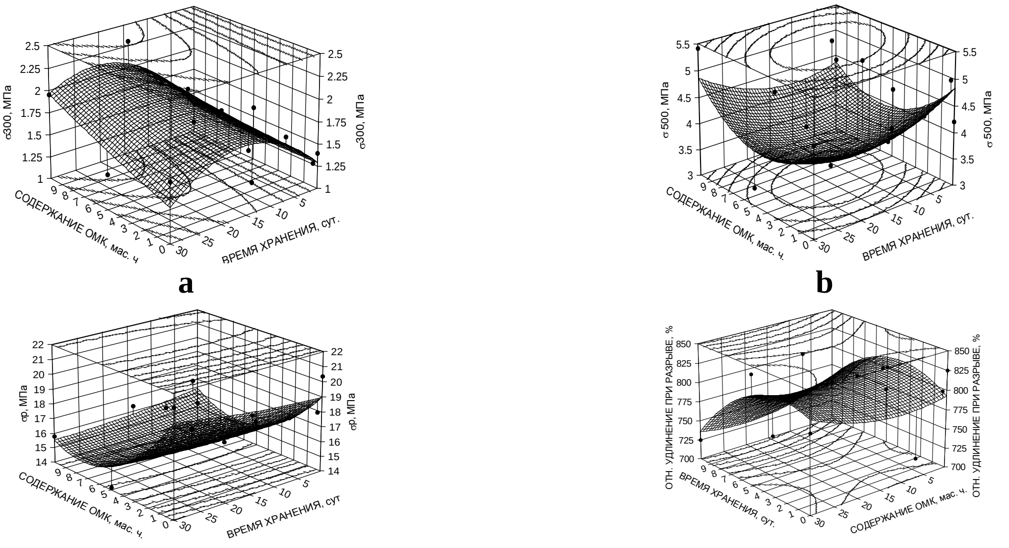
Currently, to the adhesive composition on the base of elastomers is presented a series of requirements: good adhesion to various substrates, high strength characteristics of the glue film, its elasticity. Heat resistance is also a lot of importance to the adhesive joint. Considered the polychloroprene replacement on the domestic brands of butadiene-styrene thermoplastic elastomers (BSTEP). It should be noted that BSTEP are only the basis for adhesives and exhibit the adhesive properties only by their modification, whereby a significant improvement as adhesion and performance is achieved [1].It is shown that as the possible introduction of modifying additives of various resins (such as petroleum resin (NSP)), as well as agents promoting action (hinolovye esters (HE), and oligomeric metal complexes (OMC)) [2]. A considerable increase in bond strength when using a combination of modified-controlling additives for various operations using as substrates of rubber and fabric is shown. It is found that the usage of oligomeric metal complexes can significantly improve the heat resistance of the adhesive joint (up to 110°C) while maintaining the required level of a set of physical and mechanical properties of adhesive films over time (Fig. 1).



a **b**

c **d**

Fig. 1. Dependence of the glue films physico-mechanical properties from the OMC content by the different time of sample holding: a – stress at 300% elongation, b – stress at 500 % elongation, c – tensile strength, d – elongation at break.

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OBTAINING NITROGEN-CONTAINING COMPOUNDS FROM POLYETHYLENE TEREPHTALATE WASTE

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Polyethylene terephtalate (PET) is a polyester, polycondensation product of terephthalic acid (or its dimethyl ester) and ethylene glycol. PET is used for fibers, food films, and plastics.

The increasing worldwide usage of PET, along with economic and ecological pressures, has caused post-consumer or waste PET recycling to be very urgent. By the preliminary estimates, polyethylene terephtalate is the main part of total amount of polymeric waste [1].

Increasing volumes of these waste, their high resistance to the atmosphere, their poor bio- and photo degradability cause them to start accumulating in earth [2].

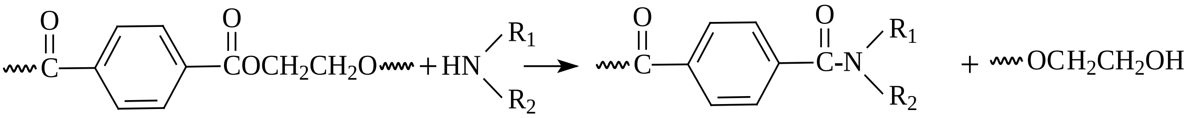
The recycling of polymers allows obtaining large range of raw components for industry. One of the approaches is the chemical (tertiary) recycling – the process leading in total depolymerization of such polymer as PET to the monomers, or partial depolymerization to oligomers and other chemical substances. The monomers could be repolymerized to the original monomers [3].

At the same time resource base expansion and cost saving are of current importance for nitrogen-containing reagents of complex action for different industries. Usage of PET waste as raw material furthers resources and energy saving, and solves environmental problem described above.

We offer the recycling of PET by aminolytic reaction with primary or secondary aminoalkanes aimed at producing a reagent of complex action for petrochemical industry.

The calculated amount of previously grinded, washed and dried PET scrap (plastic packing) and aminoalkane are loaded into a reactor. Then the reactor content is heated to desired temperature and kept for required time depending on aminoalkane. At the same time vapor condenses in reflux condenser and returns to the reaction zone.

Proceeding aminolisys of PET could be presented in following general form:



As the process is in progress changing of reaction mixture color and transparency is observed. High degree of polyethylene terephtalate conversion peculiar to the reaction.

Upon completion, product mixture is discharged out of the reaction and cooled to room temperature. It is a mixture of reaction product, ethylene glycol and non-reacted amine. The next stage is isolation of the target crystalline product.

Obtained nitrogen-containing products of PET recycling consider to be used as reagents of complex action. At present rust-inhibiting and biocidal properties of these products are being investigated.

This work is carried out with the support of grant No. B14-22 from Sterlitamak Branch of Bashkir State University.

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CONTROLLING OF BIODEGRADATION PERIOD OF COMPOUND MATERIALS BY MODIFYING THEIR COMPOSITION AND MORPHOLOGY

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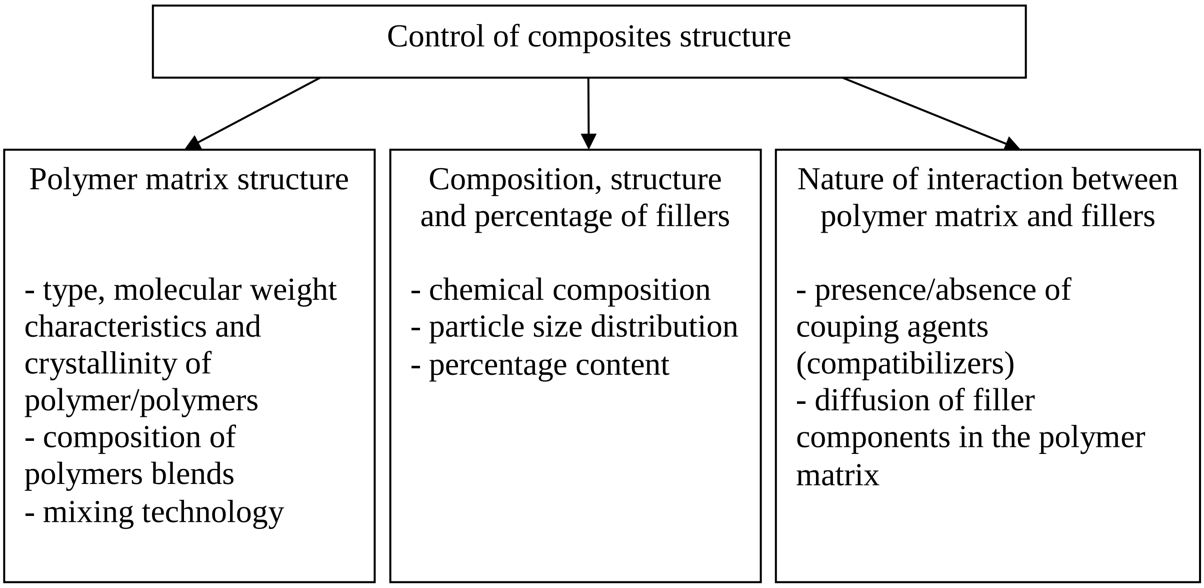
The problem of polymer wastes is actual today. The promising way of solving this problem is to create biodegradable polymer materials. Compounding of popular synthetic polymers with natural fillers can not only create biodegradable materials, but also control their biodegradation period, changing their composition and morphology. The factors influencing the composites structure are shown in the figure below.



Control of composites structure

Polymer matrix structure

- type, molecular weight characteristics and crystallinity of polymer/polymers
- composition of polymers blends
- mixing technology

Composition, structure and percentage of fillers

- chemical composition
- particle size distribution
- percentage content

Nature of interaction between polymer matrix and fillers

- presence/absence of couping agents (compatibilizers)
- diffusion of filler components in the polymer matrix

The influence of the polymer matrix structure and dimensional parameters of the filler particles on the composite morphology and, as a consequence, its biodegradability were investigated. Objects of the study were double and triple compounds, in which the polymer matrix were low density polyethylene (LDPE), isotactic polypropylene (iPP), their mixtures; the fillers – flax shive, sunflower husk, cellulose, hay, etc. with/without the addition of couping agents.

It has been found that the changing polymer type and polymer matrix composition has a significant influence on the process of biodegradation. Since using polymer blends in different weight rating as a polymer matrix made possible to vary rodlike chain ratio, crystallinity, segmental mobility in the amorphous regions of the polymer matrix. Nonregular distribution of the filler particles in the polymer matrix leads to the uneven biodegradation of composition. Therefore, couping agents (compatibilizers) were introduced to create a composition with a uniform distribution of the filler particles and improve the mechanical characteristics of the material. The influence of these additives on the biodegradability of the composite material have been revealed. Chemical composition, particle size and shape of the composite fillers are also factors affecting the material biodegradability. The presence of a large fraction of particles and protein content contributed to the fast biodegradation. Furthermore, it was shown that there is a diffusion of low molecular weight components of certain fillers in a polymer matrix during compounding.

STUDYING THE EFFICIENCY OF ACTION OF THE 4,4′-BIS(2,6-DI-*tert*-BUTYLPHENOL) IN RUBBER BASED ON NATURAL RUBBER

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Amine antioxidants are traditionally used to stabilize the operational properties of rubbers. Due to the tightening of sanitary and hygienic norms in this field, phenolic stabilizers are finding increasing application [1]. In this row 4,4′-bis(2,6-di-*tert*-butylphenol) has worked well [2].

Physical and mechanical properties of rubber based on natural rubber including various stabilizers

Stabilizers	4,4′-bis(2,6-di-*tert*-butylphenol)			N-(1,3-dimethylbutyl)-N'-phenyl-*p*-phenylenediamine (6HHD)		
Index	Before aging	After aging	Relative change of index	Before aging	After aging	Relative change of index
Tensile strength, MPa	19	17	0,89	18	16	0,89
100% tensile modulus, MPa	2,89	2,23	0,77	3,40	2,64	0,78
Elongation at break, %	336	433	1,31	291	381	1,31
Hardness	76	80	1,05	75	78	1,04

In the article was studied the effectiveness of 4,4′-bis(2,6-di-tert-butylphenol) in the rubber based on natural caoutchouc (Table). The amount of stabilizer is 1 part by weight per 100 parts by weight of caoutchouc. Test results showed that the effectiveness of the 4,4′-bis(2,6-di-tert-butylphenol) is at that of the known amine stabilizer 6HHD.

Development of modern energy- and resource-saving technologies of the 4,4′-bis(2,6-di-*tert*-butylphenol) [3] allows to speak about the prospects of using this stabilizer.

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MASTERBATCHES FOR BUILDING MATERIALS BASED ON UREA-FORMALDEHYDE RESINS

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The main goal – the development of technology for compounding and masterbatch for creating high-performance building materials based on urea-formaldehyde resins. Emphasis is placed on the choice of modifiers, including nanoscale, and fillers of different nature, members of the masterbatch. The conditions with the combination of urea-formaldehyde resins developed by masterbatches (ultrasound and vibrocavitation). Defined complex technological, operational and technical properties of wood-plastic composites and insulating materials based on urea-formaldehyde resins, modified developed by masterbatches.

Research directions in the field of masterbatches for urea-formaldehyde resins, developing foundations of chemical urea filling insulating materials research patterns of hybrid binders for wood-plastic composite building materials (chipboard, fiberboard, (OSB), plywood) on the basis of urea-formaldehyde resins, and the search for a fundamentally new nanomodifiers, allow to set and fundamentally new challenges, open new avenues of research/

Possibility of synthesis of urea-formaldehyde resins is limitless, but the feasibility of putting limits its practical implementation, giving way to greater opportunities physico- chemical and physical modification. Construction is main industry of the country, based on a wide range of materials, combining the requirement to all their diversity is a large-capacity, due to the scale of construction projects, the availability of raw materials, combined with a relatively low cost.

Various sources provided extensive information about the modifications urea-formaldehyde resins. The main objectives of the modification of urea-formaldehyde polymers are to improve strength, reduced water absorption and shrinkage strain, reduction of free formaldehyde and increasing Fire safety of building materials based on them (chipboard and plate materials, oriented strand board, plywood, and urea-formaldehyde foams, etc.).

Regularities and mechanism of urea-formaldehyde resins developed by modifying masterbatches to obtain building materials of new generation. The scientific basis of new technological methods of modifying building materials based on urea resin masterbatches. Component selection was done and developed new methods for the preparation of masterbatches based on natural and man-made materials, new ways of introducing nanomodifikatorov in urea binding.

Key Benefits – improving operational and technical properties of building materials based on urea-formaldehyde resins (increased strength characteristics, reduced water absorption , reducing shrinkage and a sharp reduction in formaldehyde emissions) .

The first results of complex modifications masterbatches insulating material based on urea-formaldehyde resin – urea foam. With constant technological parameters (viscosity and gel time) have increased compressive strength carbamide resin 40-60%, improve the resistance to aggressive environments and heat resistance by 30-40%. Found that the use of masterbatches designed, does not affect the rheological properties of urea formaldehyde binder or on its adhesive properties in the manufacture of OSB, OSB, plywood. The main thing - there is a sharp reduction in the amount of free formaldehyde in the cured polymer and products based on it (7-9 times), which corresponds to the European standard class E1. It does not require capital expenditures, and implementation is limited prescription and regime activities with little interference in the production line equipment.

COMPOSITE MATERIALS BASED ON NEW POLY(ARYLENE SULFIDES)

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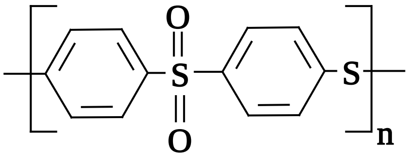
Investigation of poly(arylene sulfides) formation reaction, their structures and properties is determined the necessity in plastics having thermal and chemical stability. In this work we have synthesized new poly(arylene sulfides) with sulfone and sulfoxide groups in main chain (1 and 2):



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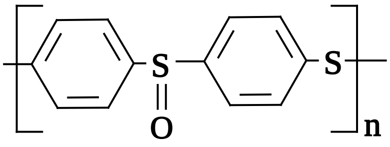

2

On base poly(phehylene sulfone sulfide) 1 we have developed a strong chemical resistant composites with filler content (silicon carbide) 85%, which could not be achieved with other types of binders. These chemical over persistent materials were designed to operate at high temperatures in the phosphoric acid fuel cell.

Chemical aspects of poly(arylene sulfide)s synthesis, their structure and properties are discussed in this work also.

MODIFICATION OF PROPERTIES OF CHEMICALLY CROSS LINKED POLYETHYLENE

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Closed cell foams based on chemically cross-linked polyolefin are mainly used in industry and household as sealing and cushioning materials. Commercially available brands have a relatively narrow compression modulus range. Whereas, in case of increasing rigidity, those materials could be used to manufacture lightly loaded products, while stiffness reduction could expand the scope of application as a structure damping elements.

By simply changing the concentration of crosslinking and foaming agents it is not possible to solve this problem. In this paper, the effect of physical and mechanical properties of the polymer matrix on the properties of chemically cross-linked polyolefin foams was studied. Low-pressure (high density) polyethylene and high-pressure (low density) ethylene copolymers with the polypropylene in the mixtures thereof were studied. Foaming composition containing in addition to polymers a chemical blowing agent (azodicarbonamide), an organic peroxide and azodicarbonamide decomposition activators were prepared on the roll mill at 110°C. Foamed samples were prepared by one-stage press technology on a hydraulic press at 170°C.

The correlation between properties of the polymer material and the foam based thereon was educed. This is probably due to the fact that in case of foam manufacture by press-technology the exactly the opposite of requirements were specified to the polymer matrix: high resilience (to provide for blast molding and foam bubbles growth without macro and micro fractures) and, at the same time, the ability to fix the foam structure in cooling.

As the study has shown, foam structure fixation is largely provided for by chemical crosslinking. However, the foam formation and bubble growth process, as well as mechanical properties of the foam depend on the viscoelastic properties of the polymeric material. Consequently, using the same blowing and crosslinking agent concentrations polyolefin mixtures based foamed plastics can be produced that sharply differ in their mechanical and thermal properties. For example, developed foamed plastics with similar apparent density differ by two orders of magnitude of the compression stress at 25% specimen deformation. At the same time the value of the stress at break of chemically cross-linked polyolefin based on low-pressure (high-density) polyethylene is not more than three times higher than when ethylene-propylene thermoplastic polymer is used as the basis. It is of interest that all the studied materials differ little from each other with regard to the residual strain after 24 hours 50% compression followed by one hour recovery.

ADHESION PROPERTIES OF FLUOROPOLYMER THIN FILMS MODIFIED BY GLOW DC DISCHARGE

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Previously, it was shown that the action of dc discharge on the fluoropolymer surface leads to a considerable decrease in contact angles (θ) and an increase in the surface energy of polymers, that is, to a noticeable hydrophilization of their surface.

For quantitative measurements of adhesion properties of thin fluoropolymer films modified by dc discharge we developed the special technique based on the ASTM D3359-02 method (T-peel test). By means of this method the studying of the peel resistance (***A***) for some fluoropolymers was carried out. The objects of study were samples of a commercial polytetrafluoroethylene (PTFE), tetrafluoroethylene-hexafluoropropylene copolymer (FEP), tetrafluoroethylene-perfluoropropylvinyl ether copolymer (PFA), poly(vinylidene fluoride) (PVDF) and tetrafluoroethylene-ethylene copolymer (ETFE) films with a thickness of 40–80 μm (OAO Plastpolymer, St. Petersburg). The peel strength of both the untreated and modified films was measured by the T-peel test method. The data obtained are presented in Table.

Fluoropolymer	The treatment	***A***, N/m		
		After treatment[1]	After storage[2]	After heating[3]
PTFE	–	30±6		
	At the anode	200±10	189±9	168±9
	At the cathode	134±4	78±5	81±8
FEP	–	33±4		
	At the anode	162±14	177±14	63±7
	At the cathode	153±8	154±15	75±8
PFA	–	34±5		
	At the anode	202±12	179±9	132±9
	At the cathode	144±9	120±8	104±9
PVDF	–	95±4		
	At the anode	133±8	143±8	113±9
	At the cathode	166±12	167±17	93±8
ETFE	–	61±4		
	At the anode	188±5	140±10	127±7
	At the cathode	212±17	166±12	94±7
Scotch®810/Scotch®810		198±5		

[1]air, 20 Pa, 50 mA, 60 s. [2] 14 days under room conditions. [3] 100ºC, 30 min.

The results of T-test show that the adhesive bonding strength of the dc discharge treated films of fluoropolymers substantially increases.

This work was financially supported by the President of the Russian Federation under the program of Leading Scientific Schools (grants NSC-324.2012.3 and NSC-1683.2014.3).

ADVANCED NANOSTRUCTURED SURFACES AND PARTICLES: APPLIED ASPECT

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Various surfaces that show superhydrophobic and ultralow-adhesive properties are very promising for a large scope of industrial and domestic applications, such as: self-cleaning surface of solar panels and car windscreens, stain-resistant textile and leather, anti-graffiti coatings, aircraft anti-ice treatment, and biofouling-resistant coatings for marine vessels. As a consequence, knowing colloid-chemical principles of formulating such special surfaces and coatings is becoming crucial for their practical implication.

Wettability regulation of a surface as well as adhesive properties can be formulated in terms of contact angle, interfacial tension(s), surface morphology and roughness. Surfaces, which show a water contact angle 90° or more, are considered to be hydrophobic. Surfaces showing a water contact angle greater than 120° are impossible for ideally smooth current materials, so they are considered as superhydrophobic.

Superhydrophobic properties are intrinsic for many natural objects, such as lotus leaf and water strider feet. Besides consisting of hydrophobic materials (e.g. cuticular wax), surface of the object has micro- and nano-relief. This two-level surface roughness is not allowing a liquid drop fit tightly to the surface and creates air pockets beneath, so the drop lies on the surface like a yogi on nails. Nowadays, creation micro- and nano-roughness on hydrophobic surfaces is a top high-tech approach in engineering of numerous nanostructured superhydrophobic and oleophobic surfaces. Formulating of the proper relief by plasma or laser treatment, mechanically or chemically is possible now for various surfaces.

Recently, developing innavative product, namely leather protector against anti-icing reagents and water, was performed by authors for the world market. Surface deposition, film-forming and segregation of moderately compatible hydrophobic ingredients are main steps in creating the very effective spay shield.

There is renewed interest to Pickering emulsions, emulsions stabilized by solid particles. They are impressive example of a nanostructured colloidal dispersion, which found now numerous applications. Instead of conventional emulsifiers, hydrophobically modified solid particles of nano-clay or nano-silica offer cost-effective and eco-friendly alternative in emulsification. The formation, stability and morphology adjustment of the Pickering emulsion become state of the art technology for the last decade e.g. in manufacturing hybrid polymer particles and nanocomposites with unique properties. So, emulsion polymerization and suspension polymerization using Pickering emulsion allows preparing in situ unusual latexes, reinforced nanostructural polymer composites, and microcapsules for topical drug delivery with unique properties.

Janus particles are another recent implementation of bifunctional nano- or micro-particles whose surfaces are different from diverse sides due to the varied chemical composition and physical properties. Janus particles got the name by association with the two-faced Janus, Roman God. These particles may be of inorganic nature (silica, iron oxide, bentonite, silver, etc.), organic nature (latex, block-terpolymer, molecule of asymmetric dendrimer, etc.), or composites.

Over the last decade, several methods of preparing Janus particle dispersions were proposed. These methods are classified into three groups: 1) nucleation and particle self-assembly in a solution (including colloidal one) or in a gas phase; 2) preparing from the (semi)finished particles using the surface modifying agent or an asymmetric build-up of an unlike nature; and 3) combination of these two methods using a particle precursor, which is created, for example, by the phase separation or self-assembling.

They may have different geometries and various surface functional groups. The surfaces may vary often in electric/dielectric properties or in the surface wetting due to unlike nature of the surface-forming hydrophilic and hydrophobic groups assembled on the different side. This anisotropy imparts to the particle amphiphilicity anisotropy, similar to surfactant molecules. Unique surface and self-organization properties of Janus particles can found a number of promising applications, like as manufacture of the (super)hydrophobic/hydrophilic layers, non-stick coatings, specific photo-switchers or stabilising surfactant-free dispersed systems.

Considered laws and approaches to creating superhydrophobic and oleophobic surfaces as well as stabilizing particles synthesis for Pickering emulsions, including Janus-particles, are illustrated by experimental results of research crew of the colloid-chemical department. Therefore, applied surface and colloid chemistry gained now a new breath with the advent of demand for advances nanostructured surfaces and nanoparticles for creating special high-tech materials.

LOW TEMPERATURE POLYMERIZATION OF METHYL METHACRYLATE VIA REVERSIBLE ADDITION-FRAGMENTATION CHAIN TRANSFER

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Studies in the field of living/controlled radical polymerization are actively conducted in recent years by different scientific schools all over the world. Unique possibilities of carrying out controlled synthesis of polymers with different macromolecular architecture and with predetermined molecular weight characteristics provide huge interest in this field. Reversible addition-fragmentation chain transfer (RAFT) polymerization has been shown to be an effective technique to produce a wide variety of polymeric architecture. These advantages are associated with efficiency, simplicity and universality. However widespread implementation of this process is constrained by its significant disadvantages like high temperature polymer synthesis, and inhibition and deceleration of the polymerization process. We have proposed a RAFT agent from trithiocarbonates class. It provides not only control of the molecular weight characteristics of polymethyl methacrylate, but also a high polymerization speed, comparable to the speed of "usual" radical polymerization. From practical standpoint it is very important that the polymerization of methyl methacrylate with trithiocarbonate proceeds under relatively mild temperature conditions (30–50ºC). And exists to produce polymers with high molecular weights comparable to the molecular weight of the so-called "molding" polymers which processed through the melt or solution. Polymerization of methyl methacrylate flew with all the characteristic features of living/controlled radical polymerization in a wide range of concentrations of RAFT agent. The characteristics like linear increase of the number average molecular weight with conversion, and low polydispersity of the polymers obtained parameters. The high efficiency of the polymer RAFT agents was shown.

PET RECYCLING PROCESSES

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The recycling of PET, primarily from beverage bottles, is a fastest growing industrial process in Russia. A volume of PET waste in Russia is 10.2 million tons at year. Many recycling PET technologies are not perfect or not developed yet.

Thermal degradation of PET is the most inefficient and no ecofriendly process. The mechanical method is include sorting and washing the bottles, grinding into flakes, washing the flakes, removal of labels and caps, and drying the flakes, melting or extruding the flakes into PET pellets. The secondary PET produced this way is suitable only for fibers and non-food contact bottle applications because it has a low density and polluted other polymers. Chemical ways of PET recycling consist in depolymerization the chemical structure of polymer with alkaline hydrolysis, methanolysis and glycolysis. Chemical methods demand significant expenditure energy and additional chemical reagents, but in the chemical method can be used raw materials of low quality, due to an additional chemical purification.

In this work we study a PET recycling process by glycolysis with the different catalyst systems.

Glycolysis reaction was carried out in a glass reactor. PET granules are prepared from purified, washed and crushed bottles. Reactions proceed at temperature 190-200^{o}C and an atmospherically pressure. We used ratio of the components PET : ethylene glycol = 1:3 (by the weight) and catalyst content were of 1% from the reaction mass.

We carried out the series of experiments without catalyst and in presence the barium hydroxide, sodium hydrogen carbonate and zinc acetate. The quantitative analysis of reaction products was carried out using titration (containing ester groups). PET conversion was experimentally determined by yield of terephtalic acid on alkaline hydrolysis of the reacting mass.

Yield of terephthalic acid without a catalyst at reaction time 20 hours was 2.1 g; of barium hydroxide at reaction time 7,5 hours – 1,3 g; of sodium hydrogencarbonate at reaction time 6 hours – 4.5 g; of zinc acetate at reaction time 3 hours – 4.7 g

Thus, the use of zinc acetate as a catalyst enables to obtain the highest yield product of reaction. In the proposed PET recycling process we not need to isolate terephthalic acid or catalyst because the reaction mass can be directly used as a feedstock for the production of polymer. The advantages of proposed PET recycling process are using of economical raw materials, reagents, available and not expensive catalysts.

NEW METHODS OF MODIFYING OF SYNTHETIC FIBER MATERIALS TO IMPROVE THEIR QUALITY AND TO GIVE NEW PROPERTIES

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Today, extensive investigations are being performed that aim at creating the physicochemical foundations for fiber modification that would allow production of fibrous materials, in particular, synthetic ones possessing a predictable combination of special application properties.

The problem of modification of conventional synthetic fibers is difficult, since the fibers development of the production of which is of high priority (polyester, polypropylene) feature high chemical resistance and structure density. One promising way to modify thermoplastic fibers seems to be the immobilization of a modifying agent in the fiber material via its introduction into the melt of a fiberforming material.

Investigations of the application of ultradisperse polytetrafluoroethylene (PTFE) for modification of polypropylene filaments at the molding stage in order to improve their qualitative characteristics were made at the G.A. Krestov Institute of Solution Chemistry of the Russian Academy of Sciences (Ivanovo) [1,2]. We studied in detail the structure and properties of modified polypropylene thread. As was found, the introduction of 1–2% ultradispersed PTFE, which is retained in the matrix polymer as an individual phase, into polypropylene filaments during spinning significantly improves the values of relative tensile stress and elastic modulus of the filaments. Moreover, it was established that the modification increases the roughness and hydrophobicity of the polymeric material.

The basic characteristics of polypropylene filaments, modified by nanoscale metal species immobilized in a high-pressure polyethylene were investigated. We established that after introducing of trace amount of powder particles of metal into the polypropylene melt, it’s possible to notice an increase of a relative tensile load of polypropylene yarns without reducing of permanent strain after rupture and deterioration of tribological characteristics of the yarns. The most significant increase in strength was stated when using iron, manganese and nickel composites. It is shown that after yarns modification by trace amount of nanoscale metallic particles a considerable (10^5 - 10^6) reduction of the surface electrical resistance of the yarns occurred whereas the use of industrial antistatic agents provides a reduction of this parameter in 10^4 times only. We revealed that polypropylene filaments, modified by nanoscale particles containing transition metals, have an inhibitory effect on the development of all types of pathogenic microorganisms. The strongest activity of Gram-positive, Gram-negative bacteria and pathogenic micro fungus is reduced when using small amounts of manganese and iron nanocomposite powders.

We also devoted great emphasis to fiber modification for giving polyester textile materials high water repellency. We have shown the possibility and effectiveness of modification of polyester fibrous materials via formation on the surface of their constituting fibers of a nanosized coating based on low-molecular-weight polytetrafluoroethylene [3]. The coating imparts to the fibrous material a high hydrophobicity intrinsic to the fluoropolymer. The surface fluoropolymer film replicates the rough microrelief surface pattern of the fibrous material. Preliminary chemical modification of the fibrous material, resulting in increased roughness, can also contribute to enhanced hydrophobicity. Small (nanoscale) thickness of the coating is responsible for its high stability under conditions of use.

This study was financially supported by the Russian Foundation for Basic Research (project No. 08-03-12152-ofi, 11-03-12048-ofi-m and 13-03-12065-ofi-m), by the program of the Presidium of the Russian Academy of Sciences "Support of Innovations and Developments" (2009– 2011).

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TECHNOLOGICAL CAPABILITIES TO INCREASE STRENGTH OF CARBON FIBER REINFORCED PLASTIC BASED ON THERMOSET BINDER

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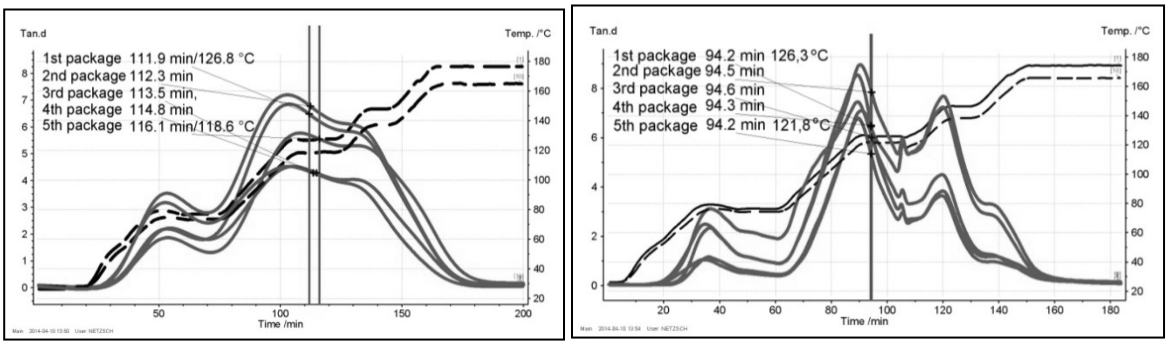
This paper is devoted to methods of improving the technology of polymer composite materials (PCM).

In the paper [1] considered the causes and effects which lead to the formation of internal stresses in polymer composites obtained from thermoset epoxy binder by vacuum-autoclave molding.

In the presented work, the possibility of increasing of strength of the material was considered by eliminating the negative effect of the temperature gradient on the velocity of curing process in the different layers of the prepreg. For this aim was investigated carbon fiber reinforced plastic (CFRP) which is made of unidirectional carbon tape and thermoset epoxy binder with amine hardener.

Analysis of the curing process of CFRP was made by using dielectric analyzer NETZSCH DEA 230/10 Epsilon with using filtered IDEX sensors. Theoretical and methodological aspects of the dielectric analysis described in [2]. The prepreg consisting of fifteen layers was divided into five packages of three layers each. The figure 1 shows curing data.



a b

—— tangent delta; ------ temperature

Fig. 1.- Data of dielectrical analysis of the process of curing of epoxy-carbon composite material:
a – non-modified, b – modified.

The uniform curing across the thickness of the material is achieved with the injection of calculated concentration of curing catalyst in the defined prepreg layers. As seen from the graphs the gelation points (which are marked as “+” on curves of tangent delta from time) of non-modified plastic are occurred with significant delay, whereas in the modified pattern, they are occurred almost simultaneously.

The resulting samples were subjected to destructive tests. According to the test on a 3-point bending strength of the modified samples increased by 20.6%, while the anisotropy of strength properties decreased by 15.6%.

The study was supported by RFBR, research project No. 14-08-31294 мол_а.

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STRUCTURAL CHARACTERISTICS OF THE ORGANIC-INORGANIC MATERIALS (CO)POLY(TITANIUM OXIDE-OXOETHYLMETHACRYLATE)

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Nowdays the new polymer composites containing nanoparticles of metals or their oxides, as well as nanostructured hybrid organic-inorganic composites have been developing. Interest to these objects is very strong because the transition from micro- to nanoparticles leads to subsize physical, chemical, structural, catalytic and biological properties of materials. Among the hybrid organic-inorganic polymeric composites the particular interest is represented by the materials based on poly(titanium oxide). It is known that the gels of poly(titanium oxide) have demonstrated unique optical properties such as reversible conversion $Ti^{4+} \leftrightarrow Ti^{3+}$ under UV-irradiation. This process is accompanied by darkening of the enlightened samples and further theirs discoloring after the end of irradiation. However the instability and absence of shape of these gels determine the need for synthesis of solid-state samples which can withstand mechanical handling. In this regard the synthesis of hybrid copolymers contained poly(titanium oxide) component which stabilized by polymeric matrix of organic nature are promising.

The aim of this research is the synthesis of organic-inorganic copolymers based on titanium isopropoxide and hydroxyethylmethacrylate (HEMA) with different ratios of monomers, the study of theirs structure, optical and catalytic properties. The organic-inorganic copolymers were synthesized by two-stage method: at first – hydrolytic polycondensation $Ti(OPr^i)_4$ in vinyl organic monomer and at second – radical polymerization of last. The obtained materials demonstrate the stability of form. The structure of hybrid nanocomposites was investigated by three methods: small-angle X-ray scattering, X-ray diffraction analysis, and secondary-ion mass spectroscopy. It is determined that at the stage of hydrolytic polycondensation the poly(titanium oxide) forms clusters with an average size of 4-6 nm and narrow size distribution. The comprehensive approach to the clusters structure investigation has revealed that they have an anatase-type crystal lattice. Clusters are chemically bonded to the HEMA organic fragment containing double bonds, which participate in the subsequent system polymerization. The quantum chemical method was applied for investigated the molecular structure of poly(titanium oxide) nanoparticles grafted to organic polymer, thermodynamic and spectroscopic characteristics of nanocomposites. The structures of poly(titanium oxide) grafted with organic groups $Ti_nO_m(OR)_x$, n = 1-5,8; m = 0,2,4,6,8; x = 4,6,8, R =-O-CH_2CH_2-OC (O)-C (CH_3) = CH_2 were chosen accordingly to simulate a linear, flat - mesh or bridging groups tetrahedral Ti-O-Ti. Method B3LYP/6-31G(d,p) were carried out for full geometry optimization of the cluster vibrational frequencies and thermodynamic parameters. The calculated frequencies and infrared intensity optimized structures were compared with the experimental IR spectra of nanocomposites. The results show that the presence of bridged structures Ti <OO> Ti leads to a broad intense band at 650 cm^{-1}, which is shifted to 600-550 cm^{-1} for increasing the number of bridges in the molecule. Tetrahedral structure give very intense double bands with maxima at 750 and 850 cm^{-1}. Linear chain Ti-O-Ti give rise to bands of relatively low intensity in the range of 850 cm^{-1}.

All the composites were characterized by the high optical transparency up to 93% in visible light region, tensile strength up to 7 MPa, thermostability up to 240ºC and demonstrate the unique optical properties - the reversible darkening of the sample due to the transition $Ti^{4+} + e \leftrightarrow Ti^{3+}$ under UV-irradiation. The photocatalytic properties of the hybrid organic-inorganic copolymers were investigated on the model reactions of methyl-orange decolouring and phenol oxidation.

This work was supported by RFBR grants No. 14-03-31981, 14-03-00585.

STUDY OF THE CROSSLINKING CHITOSAN – CITRIC ACID INTERACTION

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Chitosan is a biocompatible, biodegradable, mucoadhesive and nontoxic natural biopolymer. Because of these properties, chitosan is a promising candidate for the development of the drug delivery systems. Currently, a large number of papers devoted to the preparation and study of chitosan microspheres as controlled-release drug delivery systems. A standard method of preparation of chitosan microspheres is adding an aqueous solution of chitosan and the biologically active substance to the oil phase under mechanical stirring to form a W/O emulsion, followed by crosslinking. The typical crosslinking agents are glutaraldehyde, citric acid and tripolyphosphate. The aim of this work was to study the crosslinking chitosan – citric acid interaction and determination of optimal conditions of crosslinking.

Study of the interaction of chitosan and citric acid by photon correlation spectroscopy was performed by titration of a solution of a chitosan with concentration of 0.2 mg/ml by citric acid solution at room temperature and pH values of 4.0, 5.0 and 5.7. It was found that the particle size is not changed when the chitosan-to-citric acid ratio increase from 0.1 to 1.0 (w/w) at pH 4. The decreasing of the chitosan-to-citric acid ratio (X) from 0.5 to 0.1 (w/w) at pH values of 5.0 and 5.7 leads to a significant increase of the size of the particles in the system. The observed increase of the particle size indicates that at $pH \geq 5$ and the mass ratios $X < 0.5$ a complex is formed in the system due to the formation of ionic bonds between positively charged amino groups of chitosan and the negatively charged carboxyl groups of citric acid. High pH values required for complex formation can be attributed to the fact that the increasing of the alkalinity of the medium leads to the increasing of the number of negatively charged carboxyl groups, whereas the amount of the protonated amine groups of chitosan does not decrease so much. The spectrophotometric titration of a chitosan solution with a concentration of 0.2 mg/ml by the citric acid solution was carried out at room temperature and pH values of 5.0 and 5.7. It was shown that there is a significant increase in the turbidity of the system at chitosan-to-citric acid ratios $X < 0.5$, indicating that the complex is formed. This confirms the results obtained using photon correlation spectroscopy.

As it was shown above, the complex formation doesn't occur at pH 4, ratios of reagents $X < 1$ and room temperature. However, it was found that the complex is formed at pH 4 by heating (60°C) and prolonged stirring of the solution, as evidenced by an increase in the absorption at wavelengths between 220 and 350 nm. As the temperature increases from 60°C to 90^{o}C there is additional peak area of 270–330 nm. This may be associated with the formation of covalent bond between the amino groups of chitosan and carboxyl groups of cross-linking agent. Previously, such an assumption was made by Varshosaz et.al. based on the comparison of the characteristics of citric acid cross-linked chitosan microspheres, the preparation of which was carried out by the emulsion-crosslinking method at mild (60°C) and elevated (120°C) temperatures [1].

To avoid the sedimentation because of the formation of an insoluble complex of chitosan – citric acid, the pH 4 was chosen for preparation of microsphere by an emulsion-crosslinking technique at mild temperature.

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MODIFICATION OF COPOLYMETHACRYLATES AND NEW OPTICAL MATERIALS ON THEIR BASIS

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The development of modern technologies necessitates the creation of new optical materials and in particular solid-state laser active media (LAM) instead of traditional liquid LAM. These include the LAM based on dyes incorporated in transparent polymeric hosts, the most technological of which are currently the (co) polymethacrylates. The LAM are synthesized by block radical copolymerization of methacrylates in the presence of the laser dyes [2, 3]. Search of new modifying compounds for ensuring the stability of the dye molecules in the reaction system and in appropriate polymer hosts is important today.

In this paper, as stabilizing compounds for synthesis of polymeric LAM along with N N'-diphenylthiourea have been selected functionalized derivatives of thiazole and thiourea, 2-(3-phenylthioureido)-4-methoxycarbonyl-5-phenyl-thiazole and 2-allylamino-4-methoxycarbonyl-5-phenyl-thiazole, which were synthesized in Institute of Organic and Physical Chemistry named after A.E. Arbuzov .

The effect of these compounds on the kinetic parameters of the block radical copolymerization of methylmethacrylate-methacrylic acid (90:10 wt.%) in the presence of azobisisobutyronitrile as initiator and rhodamine 6G – classical of the laser dye, has been studied. Also, the spectral-fluorescence and lasing characteristics of synthesized dyed organic glasses have been investigated.

The reaction kinetics before small degrees of conversion has been studied by refractometric method. Registration of absorption spectra was carried out on a dual-beam scanning spectrophotometer «Lambda 35» (Perkin-Elmer, USA). The fluorescence spectra of the samples were measured using a spectrofluorometer Cary Eclipse (Varian, USA). Studies of lasing properties has been carried out when used as a pump source of the second harmonic of Nd:YAG laser (λ = 532 nm). Tests were carried out in a plane-parallel resonator with quasi-longitudinal scheme excitation of lasing.

An inhibitory effect of the above-mentioned thioureidothiazols on copolymerization has been found (increasing of the induction period, and decreasing of the initial reaction rate). At the same time their stabilizing effect in relation to the dye located in a copolymerizing system was established in the case of, when 2-(3-phenylthioureido)-4-methoxycarbonyl-5-phenyl-thiazole not chemically bound to the copolymer this effect is especially considerably. Furthermore, it was shown that the modification increases the lasing power and the generation photostability of samples, i.e. it increases their lifetime as new polymeric LAM.

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NEW GRADES OF ACRYLIC FILM-FORMING COPOLYMERS FOR FINISHING OF THE GENUINE LEATHER

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The film-forming copolymeric emulsions or their mixes based on esters of acrylic and methacrylic acids found broad application for the various stages of finishing of the genuine leather (priming, painting, upgrading). So for increase of strength and water resistance of acrylic film-forming copolymers into the composition of copolymer are introduced the different monomers with the functional groups capable to formation of cross-linked structures, or other monomers that give to polymer specific properties, such as acrylonitrile.

The purpose of this work consists in development of new types of ecologically safe aqueous acrylic film-forming copolymeric emulsions on base of buthylacrylat (BA), acrylonitrile (AN) and methacrylic acid (MAA), that provide the increased adhesion strength of a finishing coating, low water absorption, resistance at low and highest temperatures, to dry and wet abrasion and the necessary organoleptic properties.

Studies showed that at various ratios between BA and AN, can be obtained copolymers with a strength of films from 8 to 210 kg/см^2 and with relative elongation from 220 to 750%. Besides, the increase of AN content in the composition of copolymer leads to decrease of water absorption of a polymeric film in 24 hours from 29 to 16% of mass.

When developing of recipes of film-forming copolymeric emulsions a very important factor is the selection of emulsifiers system which ensures the stability of the reaction mixture during the synthesis and the stability of the emulsion at storage and processing. As emulsifiers have been used as nonionic surfactants, anionic emulsifiers and emulsifiers of mixed types and also emulsifiers having a high degree of sulfation which allow at low concentration in the solution provide a high ionic strength and stability of the system. Studies have allowed to optimize the composition of emulsifying systems that provide the required value of hydrophilic-lipophilic balance at which is achieved the aggregative stability of the copolymers, their stability under mechanical impact and to effect of electrolytes.

Polymerization of monomer mixture under selected conditions leads to the desired emulsions with solid contents of 37 to 40 wt. % and average particle sizes between 60 and 80 nm. The received copolymeric emulsions can be recommended for all types of finishing of genuine leather: priming and final finishing.

Thus studies and test results allowed to develop recipes of aqueous acrylic copolymer emulsions based on AD, AN and MAA for different stages of finishing of natural leathers. A low-temperature process for producing of the film-forming acrylic copolymer was developed. This process enables the production of polymer with the desired properties. The initiator and emulsifier systems were selected and monomer compositions of copolymers have been optimized. A method for reducing the concentration of residual monomers has been proposed which allows to make acrylic emulsions with low residual monomer content from 0,2 to 0,6 wt. %. Testing of technological parameters of the synthesis of acrylic film-forming emulsions on pilot plant and industrial scale has been carried out.

ORGANOYTTROXANEALUMOXANES AND COMPONENTS OF HIGH-TEMPERATURE RESISTANT CERAMIC COMPOSITES BASED ON THEM

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Ceramic composites of yttrium aluminum composition are successfully used in the rapidly developing fields of electronic engineering, space instrumentation, lighting industry, construction industry, however yttrium aluminum ceramics are obtained by sintering at high temperatures (1800–2000ºC). Therefore it is important to reduce the sintering temperature, which is provided by using ceramic forming poly(oligo)mers, from which unique heat-resistant components of ceramic composite materials can be obtained by high-tech "polymer" technology.

GNIIChTEOS researchers have developed synthesis methods of ceramic forming poly(oligo)mers – organoyttroxanealumoxanes [1] and methods of preparation binders and impregnating compositions based on them for creating high-temperature resistant, chemically resistant, yttrium aluminum oxide coatings and yttrium aluminum ceramics. As well as fiber forming organoyttroxanealumoxanes were synthesized; from their melt polymer organoyttroxanealumoxane fibers with a given molar ratio of Al:Y were produced.

The organoyttroxanealumoxanes were synthesized by co-condensation of chelated alkoxyalyumoxanes and yttrium acetylacetonate hydrate – $(CH_3(O)CCH{=}C(CH_3)O)_3Y \bullet 2{,}5H_2O$.

The general formula of organoyttroxanealumoxanes:

$$[\mathrm{Al(OR)}_l\mathrm{(OR^*)}_x\,\mathrm{(OH)}_z\,\mathrm{O}_y]_m \bullet [\mathrm{(R^{**}O)}_s\mathrm{Y(OH)}_t\,\mathrm{O}_r]_k,$$

where $m/k < 200$; $l + x + 2y + z = 3$; $s + t + 2r = 3$;
R – C_nH_{2n+1}, $n = 2 – 4$; R* – $C(CH_3){=}CHC(O)OC_nH_{2n+1}$; R** – $C(CH_3){=}CHC(O)CH_3$.

The processes of thermo transformation of the organoyttroxanealumoxanes in ceramic phases were studied.

A full cycle of physical and chemical researches (NMR, IR, DSC, TEM, SEM, XRD, etc.) both synthesized organoyttroxanealumoxanes and products of their thermo transformation in the ceramic phases was completed.

It has been established that the pyrolysis of the organoyttroxanealumoxanes at 1300–1400ºC in an oxidizing atmosphere results in the formation of yttrium aluminum garnet and corundum, i.e. such oligomers can be used for creating a new generation of high-temperature resistant, chemically inert yttrium aluminum ceramic composites with the composition of $xY_2O_3–yAl_2O_3$.

This work was supported by the Russian Foundation for Basic Research, project No.13-03-12014 ofi_m.

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CALCULATION OF POLYMERIZATION KINETICS OF PROCESS BY A MODIFIED QUASISTATIONARY METHOD

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The kinetic dependences of concentration, rate and time of polymerization process [1–3] on a basis of a quasistationary method are considered. The kinetics of polymerization, drying, hydration, dehydration and others non stationary processes may be well described by the modified quasi-stationary method (MQM).

For a quasi-stationary summation of reaction rate of simple chemical reaction type $A \leftrightarrow B$ and mass transfer the result equation may be written as:

$$\frac{dC}{d\tau} = k(C - C^*) + \beta(C_0 - C) \qquad (1)$$

For calculation on this equation it is necessary to know dependences k and β on time. At the solution of the differential equation of the isotropic diffusion with a constant boundary condition the dependence for β is found [4, 5] $\beta = \sqrt{D / \pi\tau}$.

The Eq. (1) analytically is not solved and can be solved only numerically. The problem of its solution can be simplified, that the rate of drying and the change of the concentration in due course at limit of internal diffusion are described identical equations. This idea is realized in a modified quasi-stationary method [5]. Accepting in the Eq. (1), the rates of internal diffusion and kinetics are equal, after the elementary transformations of the Eq. (1), entering the characteristic time of process $s = D/(\pi k^2)$, uniting in one variable parameters D and k, the result equation can be obtained:

$$\frac{w}{w^*} = \frac{1}{1 + \sqrt{s / \tau}}, \qquad (2)$$

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POLIYMERIC COMPOSITES FOR PREPARATION OF NIOBIUM-TANTALUM CARBIDES AND THEIR SOLID SOLUTIONS

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Niobium-tantalum carbides belong to the most unfusible materials. According to literature melting temperature of solid solutions of NbC and TaC varies with additive low in depend of their composition from 3770 K and to 4140 K respectively.

Due to a development of aviation and a missilery the obtaining of ceramic porous unfusible products by polymeric technology from carbides of niobium and tantalum with structure $Nb_xTa_{1-x}C$ ($0 \le x \le 1$) is a perspective area.

By the analysis of data and patents related to this theme it was found that the known methods of obtaining superfine and porous unfusible carbides have disadvantages, namely: a great number of operations where volatile organic compounds are used; high temperatures of carbidization (1900–2100°C) and low purity of products.

The result of researches consists in obtaining single-phase carbides of niobium and tantalum and their solid solutions synthesized at a low temperature (1200–1400^{o}C) from phenolic binding based polymeric composites. The novelty of this work is concerned with the using of mono- and bimetallic low hydrated hydroxides of niobium and tantalum $Nb_xTa_{1-x}O_{0,5\div2,0}(OH)_{1\div4}\bullet mH_2O$ ($0<x<1$) as carriers of refractory metals. These low hydrated hydroxides are amorphous phases of variable composition with high content of pentoxides.

In order to obtain of niobium and tantalum complex carbides the bimetallic low hydrated hydroxide with 51,71 mass. % Ta_2O_5 and 23,86 mass. % Nb_2O_5 was used. In this work low hydrated hydroxide, that has been heat-treated at the 900^{o}C until the total content of niobium and tantalum oxides 100 mass. % was used. The same low hydrated hydroxide of niobium and tantalum after heat-treating at 300^{o}C consisted of 90,7 mass. % of oxides.

Due to high fineness and adsorption activity of powders of amorphous low hydrated hydroxides of niobium and tantalum the single-phase mono- and bimetallic carbides in the form of porous products and powders from materials based on their polymeric composites were obtained at lower temperatures (1200–1400°C) than a prototype (1900–2100°C). The obtained carbides are characterized as solid solutions of $Ta_{0,7}Nb_{0,3}C$ in a form of a product with general porosity 77–78%, σ = 1,5–2,3 МПа, $T_{пл} \approx 4000$ K.

The results have been obtained within the framework of State task of the Ministry of Education and Science of the Russian Federation.

LISOZYME ADSORPTION ON POLYAMIDE ULTRAFILTRATION MEMBRANES: EFFECT OF TEMPERATURE AND IONIC STRENGTH

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As per current conception it is the dimension selectivity that underlie (form the basis) the separation mechanism realized during the ultrafiltration process. Though the series of specific factors takes place in case of filtration process of protein solutions. These factors depend upon composition and structure specifics of protein macromolecules, their conformation state and structure and also the nature of protein/membrane interactions. As a consequence of idea mentioned above one can conclude that adsorption processes contribute greatly into separation and transport properties of membrane materials.

The research work of lysozyme adsorption on the series of synthesized ultrafiltration membranes based on poly-*m*-phenyleneisophthalamide *(PA)*, co-polyamides with various concentration of fragments with sulfonated groups (*PA-1(-), PA-3(-), PA-5(-), PA-10(-)*) and the mixture of poly-*m*-phenyleneisophthalamide with copolymer of acrylonitrile with dimethyldiallylammonium chloride (*PA-10(+)*) has been conducted in order to determine the nature of interactions and also for the identification of parameters of their regulation in the protein/membrane system.

The occurrence of relation between adsorption capacity *(S)* of observed samples in the static conditions with the nature of functional groups and the correlation of *S* with the concentration of these groups has been found out. Obtained results indicate the significant role of electrostatic forces (attractive forces and repulsive forces) in the adsorption process mechanism in case when both protein macromolecules and the membrane surface possess an electric charge. On the other hand sufficiently high values of *S* for *PA* membrane indicate the necessity of taking into account the interactions of nonelectrostatic nature as well as Coulomb forces while predicting the adsorption capacity of observed membranes.

It has been shown that with the growth of solution ionic strength in the concerned concentration range of *KCl* (0.05–0.5 M) the membrane adsorption capacity has decreased, while the temperature increase till 40°C has been accompanied by its growth. It is supposed that the type of adsorption capacity dependence upon temperature in observed protein/membrane systems is primarily due to the significant role of hydrophobic interactions realized in them.

Based on the analysis of kinetic data obtained for statistic conditions it has been found out that the adsorption process is governed not by the diffusion of protein molecules from the solution to the membrane surface due to the concentration gradient but by molecule transition to the adsorption state on the surface of membrane sample.

First-order and second-order kinetic equations were used to describe the adsorption process. The k_1, k_2 values and the adsorption capacity of membranes at equilibrium were determined relating to observed systems.

It has been shown that the character of protein/membrane interactions and the membrane adsorption activity in the ultrafiltration process greatly affect their separation and transport properties.

The comprehension of principal laws of adsorption and separation processes in observed systems gives an opportunity to obtain membranes with high characteristics, realizing both during the filtration process of individual model proteins and of real protein mixtures.

PROCESSING OF PRODUCTION WASTES OF LINOLEUM IN PVC GRANULES

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History has linoleum and a half centuries. Nowadays, sustainable, comfortable, durable coating became very popular. Depending on the quality of the material and operating conditions linoleum can last from 3 to 30 years, and possibly longer. But the longevity of any thing contrary becomes a problem when there is a question about its disposal.

According to official statistics in 2013, large and medium enterprises produced 182.5 million m^2 linoleum. Moreover, every year, a large number of old linoleum, out-of-operation, which falls ultimately to landfills and landfilled. However, at the same time disposing these wastes tons annually are valuable raw materials for the production of new products, if they are processed.

In this regard, the JSC "Tarkett" is an active development project recycling linoleum, which is the first stage – recycling of its own production, which include: pieces, trimming edges of PVC-based coating and without it, pieces of burnt PVC coating surface, products are not appropriate quality.

Previously, such a waste chipped and sold to third parties for further processing. But since 2010, the company launched a project «Production of semi-finished products PVC recycling line», capacity of over 8000 tons / year of PVC granules which are used in the production of homogeneous floorings. Use of recycled PVC granules can reduce the cost of 1 kg of the composition of more than 80%.

Since December 2012 the company earned calender line, designed for the processing of both their own waste, and subsequently by the PVC waste, including household. The company plans to achieve capacity utilization of 7,000 tons of post-production materials PVC calender film, which instead of using raw materials will bring savings of up to 10 million € / year. Furthermore, the introduction into operation calender installation allowed to expand the product range.

In the second phase of the project on recycling linoleum - organization of return scraps of PVC linoleum outlets.

In retail outlets remains a significant amount of unsold scrap products, which are usually transported for burial. JSC "Tarkett" suggests to recover such pruning back to the factory for processing and return to the life cycle. In the long term – return out-of-operation of PVC linoleum (after its use by the consumer) to the factory for recycling.

EFFECT OF STRUCTURAL ORGANIZATION OF THE BUTADIENE-NITRILE RUBBERS ON FEATURES OF THE VULCANIZATION PROCESS

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Technological Additive – stearic acid is an activator of vulcanization accelerators, dispersant of the fillers and the ingredients of the vulcanizing system and also improves the technological properties of rubber compositions based on diene rubbers, especially fluidity. It was also observed a decrease of the activation energy of vulcanization and increasing the degree of cross linking of elastomers with increasing content of the additive.

The purpose of the work to study the effect of spreading of acrylonitrile acid units along macromolecules (NAC units) on the features of the vulcanization process of butadiene-nitrile rubbers in the presence of stearic acid.

Copolymers investigated, despite the slight difference in the isomeric composition of the butadiene part at the same content of the NAC units (18 wt. %), characterized by the ability to change its dynamic viscosity in the presence of additive. The dynamic viscosity of the copolymers: BNKS-AMN and SKN-18C most strongly decreases in the presence of ~0.5 parts by weight, and SKN-1865 in the case of 1 part by weight additive. Dynamic viscosity SKN-SNT(V) and SKN-SNT(K) does not depend on the additive content. Features and degree of change in dynamic viscosity at increasing temperature show that there is the smallest size of ordered formations of sites alternating units in the rubber SKN-SNT(V), and the highest one is in BNKS-AMN.

As a consequence, the duration of induction period of vulcanization SKN-SNT(V) and degree of cross linking its elastomers do not depend on the content introduced stearic acid. Larger nanoscale structures of the ordered formations of sites alternating units causes a linear increase in the duration of induction period of vulcanization SKN-SNT(K) at increasing additive content. Degree of cross linking of its elastomers extremely changes at ~0.5 parts by weight stearic acid. Speed of vulcanization rubber SKN-1865 and the mesh density of chemical cross-linking of its elastomers, on the contrary, decreases linearly at increasing content ofstearic acid with simultaneous increase of the duration of induction period of the process. The degree of crosslinking of elastomers is smaller than those based on the SKN-SNT(K), in spite of a higher content of *cis* -1.4- butadiene units in the rubber SKN-1865. Mesh density of chemical cross-linking elastomers based on BNKS-AMN and BNKS-1865 is smallest among those were viewed in the work. Last one decreases at increasing of the additive concentration in the simultaneous increase in the duration of induction period of vulcanization and preserving the fixed rate of crosslinking of the macromolecules.

Thus, it was found that the features of vulcanizing butadiene-nitrile rubbers containing 18 wt. % NAC units both the original and those in the presence of stearic acid are determined not so much the content of *cis* -1.4- butadiene units responsible for the cross linking of macromolecules as features of their structural organization with ordered formations of sites alternating units. Structure of macromolecules and hence structural organization rubber SKN-SNT(K) provide the obtaining elastomers with excellent physical and mechanical characteristics.

FEATURES OF THE VULCANIZATION OF THE RUBBER SKF-32 WITH ORGANIC PEROXIDES

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Organic peroxides which are used for vulcanized fluororubbers having movable chlorine, bromine or iodine, manufactured abroad. The purpose of the work to determine the effectiveness of organic peroxides which planned made in Russia.

Peroxides used for crosslinking efficiency of caoutchouc SKF-32 in the temperature range 160–170 are placed a number of descending degree of crosslinking: PDK, Novoporoks BP-40, PCG, and TBKP. The densest network of chemical cross-linking is obtained using TBKP. As you work, zinc oxide used for the absorption of hydrogen fluoride that is released during vulcanization was replaced by magnesium oxide which also absorbs hydrogen fluoride.

Magnesium oxide will increase the efficiency of cross-linking rubber SKF-32 considered organic peroxides. Replacing oxide changed the sequence of organic peroxides efficiency structuring rubber: Novoporoks BP-40 ≈ PDK> PCG >TBKP. Density network of chemical crosslinking organic peroxides are arranged in a row: Novoporoks BP-40 > PCG > TBKP ≈ PDK.

According to infrared spectroscopy, crosslinking rubber macromolecules accompanied by the appearance of new bands at swallowing 1458, 1693 and 1743 cm^{-1}. Studies have shown that in the presence of magnesium oxide three chemical reactions take place and since only one of zinc oxide. This explains the higher degree of crosslinking of the samples which contain magnesium oxide than those which contain zinc oxide. It was established that chemical processes which occur in the peroxide cure are dependent upon the nature of the metal oxide, a peroxide and a mineral carrier.

OZONE-RESISTANCE OF BUTADIENE-NITRILE ELASTOMERS AND THE CONDITIONS OF THEIR VULCANIZATION

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Nitrile rubber (NBR) is used for the production of oil and petrol resistant technical rubber intended for bundling machines and mechanisms working in hostile environments. BNK transition from the SKN brand to BNKS accompanied by decline in the quality of rubber for different purposes, and especially frost, thermal resistance and resistance to a number of aggressive environment, in particular, containing ozone environment.

The purpose of the work was to study the effect of formulation ingredients on the ozone resistance of vulcanizates based on SKN and BNKS with different content links of nitrile acid (NAC).

Application of a method of a relaxation of tension at various deformations allowed to reveal unequal reactionary ability of double bonds vulcanizates BNKS and SKN towards ozone, despite the same degree of cross-linking their content NAC close isomeric composition of the butadiene part and the same type of chemical cross-linking. With increasing temperature vulcanization in case of application Captax there is a small improvement ozone resistance elastomers SKN-18 and SKN-40 but its deterioration in case of elastomers SKN-26. When replacing Captax on sulfenamide ozone resistance of vulcanizates SKN-18 and SKN-26 decreases, but does not change in the case of vulcanizates SKN-40, despite the persistence of constant grid density of chemical bonds. Upon transition from SKN to BNKS it isn't dependent on type of the chosen accelerator of curing significantly nature of dependence of ozone resistance of their elastomers from the total contents of the cis-and trans-1,4-butadiene units, the reaction of the double bonds with ozone which causes destruction of macromolecules of BNK and growth of speed of a relaxation of tension in them. The observed dependence of the ozone resistance of NBR vulcanizates from the cross-linking conditions of macromolecules is stored in the case of their reaction with ozone in stationary conditions in thin layers. Unequal behavior of vulcanizates in ozone containing environment due to the fact that in macromolecules BNKS sequence chreda trans-1,4-butadiene units and NAC longer than in rubbers SKN, according to data obtained by X-ray diffraction. Big by the size the ordered educations created by such sequences, are reconstructed at stretching vulcanizates more difficultly that creates steric obstacles to development of process of orientation fragments of macromolecules. This process is responsible for the ozone resistance of vulcanizates in tension, according to data obtained by X-ray analysis. The validity of this position is confirmed, in particular, the lack of dependence of the ozone resistance of vulcanizates BNKS-40 from the strain, at least at relative lengthening ≤ 130%.

Thus, the ozone resistance of vulcanizates BNK strongly depends not only on the type and content of double bonds in the butadiene units, but also on the conditions of crosslinking macromolecular rubbers : temperature, the type of the accelerator, the content of stearic acid.

PRELIMINARY STUDY OF THE POST CURING PROCESS FOR THE POLYESTER GLASS FIBER REINFORCED COMPOSITES

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This study examines the influence of different post cure parameters to a glass fiber reinforced composites, based on five most frequently used types of polyester resins such as ortophtalic, isophtalic, dicyclopentadiene, vynil ester and epoxy vynil ester resins. The goal of this study is to evaluate optimal post cure parameters for different polyester resins that provide required properties for current production application.

Experimental part of study consists of polyester composite samples casting with three different cure systems, based on methyl ethyl ketone peroxide and cobalt (II) 2-ethylhexanoate. First curing system is «slow», what is meaning that exothermal peak is approximately at 60 minutes for each resin type. Second curing system is «middle» – exothermal peak is approximately at 40 minutes for each resin type. Third system is «fast» and exothermal peak is approximately at 20 minutes. These three curing systems were chosen because they are typical for most production cycles (except bulky parts production cases).

Samples of five resin types and three different cure systems that described above were post cured 22±2°C («normal» post cure conditions) within maximum three weeks. After that the other batch of samples was post cured at 40±2°C, and the last batch was post cured at 60±2°C.

For the first batch during the post cure the surface hardness and indirect polymerization degree were measured. The ending point of post curing process was when the surface hardness no longer increased for five last measures. In most cases for the production conditions it is mean that post cure process is ended. After that the flexural properties of the material were determined by 3 point bending test. These results were accepted as control data.

After that the second and the third batch of samples were casted with three curing systems and post cured as said above. For both batches the same parameters during post curing process were measured: surface hardness and indirect polymerization degree. And after post cure the flexural properties of the material were determined by 3 point bending test too. The difference between first control batch and second is in the ending point. In this way the ending point was when surface hardness reached the same value as in the first case and no longer increased for five last measures.

The results of this experiment were the correlations between resin type, curing system, surface hardness gain during post cure, indirect polymerization degree gain during post cure, mechanical properties after post cure and total post cure time.

Theoretical part of the study is to analyze these correlations and evaluate optimal post curing modes for each type of resin and curing systems. This will help to reduce the production cycle time of a post cure process and save energy for heating without losing mechanical properties of the final composite product.

POLYMERIC CATALYSTS IN THE 2nd GENERATION BIODIESEL SYNTHESIS

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Nowadays the production of fuels-from-biomass has receive considerable attention. Biomass is used as a feedstock that can replace fossil fuels for the energy production, especially for the transportation sector, which strongly depends on petroleum [1].

Biodiesel is the most prevalent kind of biofuels. Commonly the term "biodiesel" means the fatty acids methyl ethers, obtained by transesterification of triglycerides from natural oils and fats with methanol. However, there is growing concern about the fungibility of these fuels with conventional petroleum-derived diesel due to the oxidative and thermal instability.

The most promising way of biofuel obtaining in the form of saturated hydrocarbons from the oxygen-containing compounds is hydrodeoxygenation. Biofuel produced via hydrodeoxygenation is usually called the second generation of biodiesel or "Green" diesel [2]. "Green" diesel has numerous advantages such as high cetane number, good low-temperature properties, superior thermal and storage stability, and materials compatibility in comparison with both petrol diesel and biodiesel [3]. Besides, "Green" diesel is the product which does not depend on raw materials origin, and is mixing easily with common diesel fuel.

In this investigation the hydrodeoxygenation of fatty acids was carried out. The stearic acid (99%, KhimMedService, Russia) was used as the model substrate. n-Dodecane (99.9%, Sigma-Aldrich) was used as a solvent. Palladium supported on hypercrosslinked polystyrene (HPS) of MN270 type (Purolite LTD, UK) was used as a catalyst. The metal loading was varied from 1 up to 5% (wt.). The process was conducted in stainless steel batch reactor PARR-4307 (USA). The following reaction conditions was varied: hydrogen pressure 0.2–1.8 MPa, temperature 230–255^{o}C, concentration of stearic acid 0.05–0.2 M. Liquid samples were taken every hour during the process and analyzed using GC-MS.

Catalysts samples were characterized by low-temperature nitrogen physisorption, transmission electron microscopy, X-ray photoelectron spectroscopy, thermogravimetric analysis and differential scanning calorimetry.

It was revealed, that the main product of the reaction was n-heptadecane. The most effective catalyst for hydrodeoxygenation process was 1%-Pd/HPS. The optimal conditions of the reaction was hydrogen pressure 0.6 MPa, temperature 255^{o}C, concentration of stearic acid 0.1 M. The selectivity of the process (regarding to n-heptadecane) reached up to 99.9% at 100% conversion of the substrate.

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POLYMER-STABILIZED MAGNETICALLY SEPARABLE CATALYSTS – THE EFFECTIVE CATALYSTS FOR HYDROGENATION

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Magnetic NPs as supports for catalytic species attracted considerable attention because they allow easy separation of catalysts from reaction mixtures and their repeated uses, resulting in energy conservation, more environmentally friendly processes and cheaper target products.[1-3] Because magnetic properties of NPs are size dependent, narrow NP size distribution is an important requirement in magnetic NP syntheses. Monodisperse iron oxide NPs can be prepared by thermal decomposition of iron acetylacetonates or carboxylates in high-boiling solvents containing surfactants (oleic acid, oleylamine, etc.).

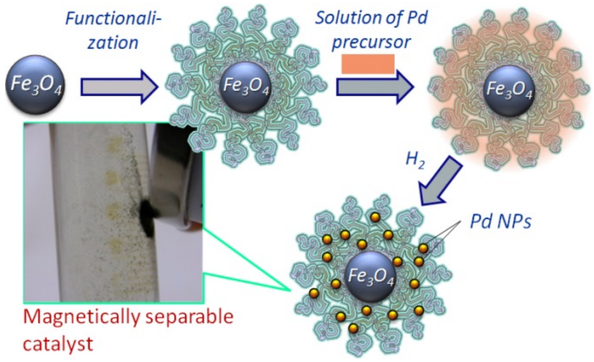
NPs can be functionalized in various ways involving surfactants or polymers, but the most facile method is a place-exchange reaction allowing one to replace regular surfactants with functional ligands on the NP surface. Iron oxide NPs are known to be well stabilized by fatty acids, such as oleic acid, containing a single double bond, but more functional groups are preferred for complexation with catalytic complexes in the magnetic NP shell.

In this talk we will discuss functionalization of monodisperse iron oxide NPs with commercially available functional acids containing multiple double bonds such as linolenic (LLA) and linoleic (LEA) acids or pyridine moieties such as 6-(1-piperidinyl)pyridine-3-carboxylic acid (PPCA). Double bonds and pyridine groups can be reacted with noble metal compounds to form catalytically active species in the magnetic NP shells, thus making them promising magnetically recoverable catalysts.

The synthesis of Pd-containing magnetically separable catalysts is presented in Scheme 1. Catalytic testing was carried out in selective hydrogenation of dimethylethynylcarbinol (DMEC) in isothermal glass batch reactor at ambient hydrogen pressure varying the solvent type, temperature and substrate loading.

We developed magnetically recoverable catalysts via functionalization of monodisperse iron oxide NPs with commercially available functional acids such as LLA, LEA and PPCA using place-exchange reaction. The NPs functionalized with LLA and LEA containing multiple double bonds were reacted with bis(acetonitrile)dichloropalladium(II) to form π-complexes involving two double bonds.

After complexation with the Pd compound both LLA- and LEA-coated NPs form NP aggregates of comparable sizes despite different structure of these acids (Fig. 1).



Scheme 1. Schematic representation of the synthesis of Pd-containing magnetically separable catalysts.

We established that aggregates are required for fast magnetic separation (within 1-2 minutes). For the NPs coated with PPCA, the latter reacts with Pd acetate leading to both intraparticle and interparticle interactions resulting in smaller NP aggregates, whose magnetic separation is slower (~5-7 minutes).

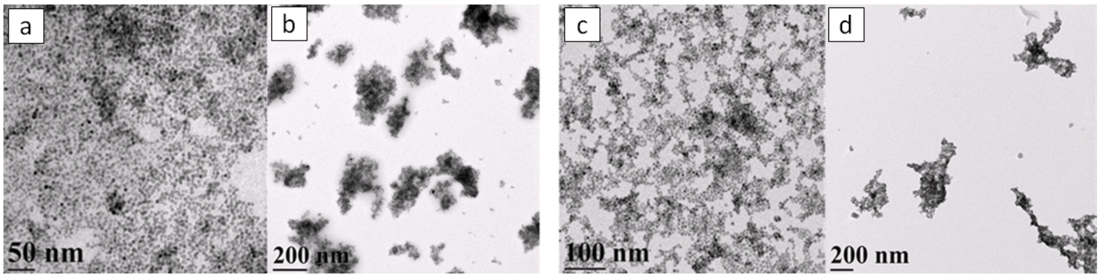


Figure 1. TEM images of NPs functionalized with LLA (a) and LEA (c), and Pd-containing samples: Fe_3O_4-LLA-$PdCl_2$ (b) and Fe_3O_4-LEA-$PdCl_2$ (d).

The high TOF of 7.9 s^{-1} and 7.4 s^{-1} were observed for Fe_3O_4-LLA-$PdCl_2$ and Fe_3O_4-LEA-$PdCl_2$, respectively, while the selectivity for the target product was higher for Fe_3O_4-LLA-$PdCl_2$ (92.5% at the 1st run and 94.4% at the 2nd use of the catalyst) than that for Fe_3O_4-LEA-$PdCl_2$ (90%). The Fe_3O_4-PPCA-PdAc catalyst, however, was found to be less active with TOF=6.3 s^{-1}. This reveals that the catalytic performance does not depend on the size of the NP aggregates because all of them are penetrable for a substrate, but rather depends on the type of the Pd environment.

The magnetic composites containing Pd species have been synthesized and tested in a model reaction of selective hydrogenation of DMEC. Easy magnetic recovery of the catalysts, high selectivity and activity along with stability of their catalytic performance make them promising for a commercial use.

Acknowledgment

Financial support was provided by the FP7 project POLYCAT (CP-IP 246095-2) and the Deanship of Scientific Research (DSR), the Russian Foundation for Basic Research and the Ministry of Education and Science of the Russian Federation.

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INTENSIFICATION OF PHENOL-FORMALDEHYDE RESINS PRODUCING

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Receipt of phenol-formaldehyde resins is the process with a large output. The volume of production in Europe is about 380 thousand tons in the year, in Russia – about 120 thousand tons per year. It is used as a binder in the production of filled press compositions with various fillers, adhesives, impregnating and coating compositions (for plywood, woven and full of fiber materials). It is also used for plastics, synthetic adhesives, paints, switches, brake linings, bearings, and widely used in the manufacture of balls for billiards.

In the process of phenol-formaldehyde resins production there are large amounts of tar-waters. In average per 1 ton of resin turns around 600–900 kg tar-water. Wastewater production of phenol-formaldehyde resins require special cleaning from phenol, formaldehyde, and resin. Regenerative and destructive practices are used for their cleaning.

The concentration of water-methanol solution of formaldehyde will reduce the amount of tar-waters and the concentration of phenol, formaldehyde, and also to intensify the process of obtaining of resin, i.e. with one reaction volume can get a higher yield of tar.

The most common method of water-methanol solution concentration of formaldehyde is rectification.

The experiments were made on the rectification of technical formalin laboratory rectifying installation in atmospheric and vacuum conditions. It showed us that for the strengthening of formaldehyde technical is preferable to the use of vacuum column, which has several advantages, one of that is the lowered temperature of the process of strengthening of formalin, which reduces the acid number of the obtained product. Also it is possible to concentrate technical formalin up to 50% and higher in vacuum, and at atmospheric only to 46%.

MODIFICATION OF THE POLYMERS ON THE BASE OF POLY-4-VINYLPYRIDINE FOR PREPARATION OF REDOX MEDIATORS

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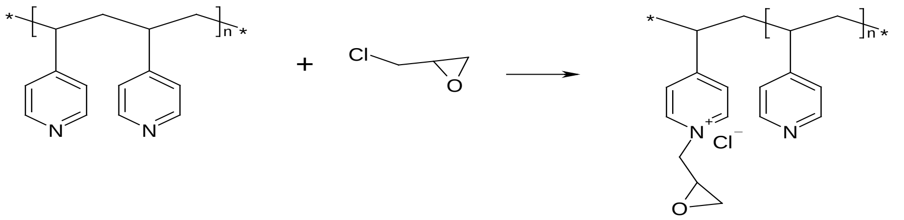
A number of polymers on the base of poly-4-vinylpyridine (P4VP), modified by epichlorohydrin (ECH) and 1-(3-aminopropyl)-imidazol (API) has been obtained for preparation osmium complexes and using as redox mediators of biosensors.

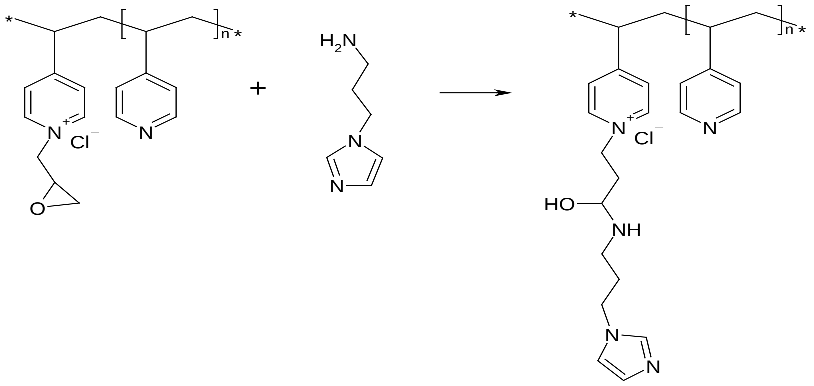
At first reaction of P4VP with ECH carried out by following method (scheme 1):



Scheme 1. Reaction of P4VP with ECH.

4.76 mmol (0.5 g) P4VP was dissolved in 50 mL ethanol in round bottom 100 mL flask. Various amounts of ECH (see table slowly was added. The mixture was heated at 50–60^{0}C with stirring overnight. Then the mixture was cooled and slowly was added to 1 L of diethyl ether. The product (1.3) was precipitated and then separated from a solvent by a decantation and the rest of solvent was evaporated by rotor evaporator. The dried product was tested by NMR (D_2O).

Modified polymers on the base of P4VP were synthesized according to following scheme 2:



Scheme 2. Reaction of 1.3 with API.

Obtained modified polymers on the base of P4VP are listed in table.

Modified polymers on the base of P4VP

Modified polymers	P4VP, mmol	ECH, mmol	API, mmol
P1	4.76	1.19	1.19
P3	4.76	1.90	1.90
P2	4.76	2.38	2.38
P4	4.76	3.33	3.33

STRUCTURE OF HEAT-RESISTANT ORGANIC-INORGANIC COMPOSITES BASED ON MQ-COPOLYMERS

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Heat-resistant silicone-polyimide composites were synthesized on the basis of polyimides (insoluble aromatic, fusible, segmented imide containing polymers) and MQ-copolymers of different chemical structure. Composites were prepared by co-dissolving in an amide or mixed solvent the synthesized imide containing oligomers or polyimide prepolymers with an organosilicon component in various proportions. The final material was obtained by heating the hybrid compositions.

According to the SEM microscopy, samples of cured silicone - polyimide composites are a system composed of a polymer matrix and dispersed therein spherical organosilicon particles. The size of particles ranges from 1 to 20 microns, depending on the contents of MQ copolymer in composite. It is shown that the formation of the dispersed phase occurs at the stage of preparing film samples during the process of removing the solvent prior to curing.

Obtained polymer composite materials possess high thermal stability (τ_5 = 480–580°C) and characterized with dielectric permittivity from 2.1 to 2.5 depending on the composition of the silicone – polyimide composites.

The study was supported by the Russian Foundation for Basic Research (grant No. 13-03-12111-ofi-m).

INFLUENCE OF ANTIOXIDANTS ON PROCESSING FOAMING OF RIGID POLY(VINYLCHLORIDE) COMPOSITE

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Poly(Vinyl Chloride)(PVC) processing and applications are not possible without additives, like stabilizers and antioxidants, since dehydrochlorination starts above glass transition temperature [1]. These thermal stabilizers in the foaming PVC composites play a dual role: act not only as heat stabilizers, but also as activators of decomposition of blowing agent azodicarbonamide (ADC), lowering the decomposition honest temperature and leading to complete gasification of ADC [2]. Similar the role hydrogen chloride which released during dehydrochlorination [3]. On the other hand products of radical decomposition ADC accelerate structuring of PVC, which in turn hinders the foaming [3].

Investigated the foaming compositions based on PVC C-6359. Azodicarbonamide (1phr) as blowing agent was used. All composites contained 4 phr per 100 phr PVC thermostabilizer tribasic lead sulfate (TOSS). Additives of additional stabilizers phenolic antioxidants, Irganox 1010 and Irganox 1035, as well as the organosilicon oligomeric hydride, Penta-804 ™ (from 0.5 to 1.5 phr) were used. Components was combined in plastograph "Brabender" at 170–175°C. Thermal stability of PVC composites was evaluated by the change melt flow index MFI in the instrument capillary rheometer at 190–220°C. Same capillary rheometer equipped with recorder of vertical driven piston was used to study the kinetics of foaming compositions at 200–220°C. Expansion factor (EF) was calculated as the ratio of the altitude tablets volume into the cylinder of the capillary rheometer before and during foaming operation.

According to the previous work [3], TOSS added to the "inert" polyethylene PE composites does not activate decomposition of ADC. Also, in PVC composites increase of content of TOSS above 3 phr does not influence on the kinetic and maximal EF reached to 2.0-2.2 at 200°C. While, used antioxidants Irganox-1035 (at concentrations $\geq$ 1 ADC phr) EF reached 3.5, which is close to the values calculated from the amount of ADC gas at this temperature EF = 4.0, and Irganox-1010 EF raised to 3.1. These antioxidants prevent the structuring of PVC and reduce the melt viscosity. Organosilicon hydride, which is antioxidant and inhibitor dehydrochlorination, suppresses foaming activity ADC in PE and PVC, and sharply reduces EF in PVC composites to 1.5–1.8.

Thus, the introduction of foaming PVC compounds phenolic antioxidants beneficial effect on the foaming process and promotes foaming expansion (EF) 1.5 times.

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STUDY OF POSSIBLE USAGE OF LIGNIN CONTAITING WASTE PRODUCTS OF WOOD PROCESSING FOR THE POLYMER COMPOSITION SYNTHESIS

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The development peculiarity of chemical processes of polymer materials and coatings synthesis compared to the other sub-sectors of the chemical industry is that this industry significantly depends on the availability of cheap and available feed sources. Current situation analysis, conducted by the authors of this work, showed that during the period from 2000 to 2014 in economically developed countries, the price for the crude oil has increased 10 times, isoprene and divinyl prices have gone up 5– 8 times. Prices for animal fats and vegetable oils for the paint industry in Russia have sharply increased up to 40–50 thousand rubles per ton. Even the wood processing products, such as raw and distilled tall oil (TO) and also fatty acids of tall oil (FATO) have gone up in price to similar values. As the result of conducted researches it was found, that in addition to traditional sources of natural feed (vegetable oil, natural rubber, cellulos, etc) and synthetic feed (crude oil, gas, coal etc) for the production of polymer and paint with greatest success there could be used the process lignin containing wastes (LCW) of tall oil, accumulated in ponds of most pulp and paper plants in Russia. However, difficulties, arising when retrieving them from ponds and complex hydrocarbon composition of LCW, constrain industrial processing methods of this practically free of charge alternative hydrocarbon feed source.

A detailed study of the LCW composition showed that all the samples taken from different ponds at different pulp and paper mills (PPM) contain water, mechanical impurities, lignin, fatty and resin acids, unsaponifiables or neutral substances and also impurities typical for products of vegetable origin.

Preliminary studies have shown that lignin contained in LCW is an aromatic substance in nature and, in a first approximation its (based on composition and properties are similar to the natural lignin, which has not been subjected to alkaline and acid treatment at PPM.

It has been established, that after the separation of the lignin from LCW and associated processing, the details of which would be announced in the report at the conference, it can be used as a binder in the production of plastic masses, glass plastics and carbon plastics, woodchip boards and fuel pellets.

It has been proved that extracted from LCW fatty acids, such as: stearic, oleic, linoleic, linolenic in their natural mixture in crude tall oil after its vacuum distillation allow to receive on their basis the "fatty acids of tall oil", which fully comply with the technical regulations on these wood-chemical products.

In further studies, it was shown that on the basis of obtained from LCW "fatty acids of tall oil" it is possible to get high-quality varnishes and paints, plasticizers for polymers, defoamers and flotation reagents. Moreover, in the framework of the present work, on the basis of obtained fatty acid fraction of tall oil, it has been performed the synthesis of alkyd resins, textile and lubricating oils, hydraulic fluids and lubricanting-cooling fluids.

Extracted from LCW resin acids (rosin) have been tested in the production of adhesives used for gluing paper and cardboard, production of varnishes, rubber products, insulation materials, detergents, in electrotechnical and radioelectronic industries.

All results of the research are confirmed by the data published in more than 250 printed works.

WAYS OF ENVIRONMENTAL PRESSURE REDUCTION IN TREAD RUBBER PRODUCTION

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Chemical and petrochemical industry relates to one of the main polluters of air basin (carbon dioxide, carbon oxide, sulfurous gas, hydrocarbon, combination of nitrogen and industrious dust of different composition and etc.), water and soil (petroleum and petrochemical products, phenol and other poisonous substances). So in 2012-2013 enterprises of chemical and petrochemical industries emitted about 1.6 mln tons of polluting substances equally to about 6% of total emission in the Republic of Kazakhstan. The given emissions caused contamination of soils by metals and other toxic substances above maximum concentration limit in the radius to 5 km around cities, where they are situated. From 2.9 km^3 of sewage water, contaminated water accounted for about 80% due to the enterprises of chemical and petrochemical industries. Problems of environment protection connected with chemical and petrochemical, in particular, rubber industry is especially actual in view of increase of share of synthetic products in chemical production, which are not decomposed or decomposed slowly in the environment. Rubber products relate to such synthetic products.

In rubber industry different natural minerals are employed mainly as fillers, rarely as modifiers or components of polyfunctional effect [1]. Positive sides of their employment in rubbers are apparent: natural minerals are ecologically safe, available, cheap and possess certain physico-chemical activity allowing to improve properties of rubber goods and mainly reduce technogenic pressure on geosystem “rubber production - environment”. According to the results of conducted research it can be said that zeolite employment in rubbers is more perspective from the above listed natural minerals. It is explained by that zeolite due to its chemical composition and structure possess unique properties: natural zeolites are porous crystals, their aluminosilicate frame is permeated by regular cavities and channels in which sodium cation, potassium, magnesium calcium lithium, barium and other are located, and water molecules as well. Except substitution isomorphism of tetrahedral atoms of the frame exists in the composition of cations. Zeolite practical employment is based on specific peculiarities in behaviour of these minerals, caused by their crystal-chemical structure and composition, exactly, correlation of SiO_2/Al_2O_3 in the composition of zeolite, and also by a kind of mineral – clinoptilolite. Zeolites are unique adsorbents. In order to realize this capacity, it is necessary to liberate the zeolite cavity from water molecules located there under the atmospheric pressure and at room temperature. Dehydration is usually realized by heating to the temperature 350ºC. Unlike adsorbents of other types zeolite frame structure predetermines strictly homogenous allocation of pores by sizes, entries to which are controlled by windows of permanent for all pores of round or oval outline [2]. Thus, zeolite effect is accompanied by several kinds of impact mechanism:

adsorption interaction between zeolite and rubber, depending from zeolite dispersion and allocation equability of it in the final composition;

chemical interaction on the line of separation of rubber and zeolite by active functional groups, herein elastomer upgrading takes place, that is strength increases, breakup and friction resistance, moreover elastomer upgrading occurs in certain optimum;

elastomer upgrading in zeolite adding is caused also by high sorption capacity of zeolites, having 50% by volume of pores and channels with developed active specific surface;

zeolite adding brings about modified supramolecular structures formation, that is supramolecular blocks of different extension, consisting of binded isoprene synthetic rubber - 3 – zeolite molecules between each other;

forming supramolecular structures have definite order in the system that results in deficiency structure decrease, responsible for vulcanization network breakup in the maintenance process, thereby zeolite adding and structure formation with less deficiency increase long term of items maintenance;

major effect from the zeolite action is connected with their unique sorption capacity.

In rubber mixture zeolites were added for partial and complete substitution of toxic raw material of white soot and technical carbon.

Formulations of tread and cushion stock with toxic components and formulation with natural minerals are shown in Chart 1.

Preparation technology of natural minerals to mixture consisted of following stages: zeolite grinding, screening and firing. Rubber mixtures were produced in two stages in rubber mixers of central laboratory of the enterprise of the “Interkomshina” JST (former Shymkent tyre plant). Zeolite was added to rubber mixture in the mixing stage. Conducted experiments showed that mixing technology, rubber mixtures processing and vulcanization in natural mineral adding don’t practically differ from standard mode, fixed in process regulation. Samples vulcanization was carried out at the temperature 155°C during 15 minutes.

For definition of zeolite effect character, its dosage in rubber mixtures is of considerable importance. In dosage less than 10 mass parts advantageously elastomer chains modification is observed, in this case zeolite will play a role of a modifier. In great dosages polymer heterophase occurs in elastomers, chemically connected with rubber and playing a role of active filler.

In employment of zeolite as filler for tread mixtures it was added to mixtures in amounts of 1-10 mass parts per 100 mass parts of rubber.

For definition of technological properties of rubber mixtures with zeolite and physico-mechanical properties of their vulcanizates number of tests were carried out according to the standard and process regulation on corresponding equipment under the plant conditions.

It is established that optimum content of modified zeolite composes 10 mass parts per 100 mass parts of rubber. Herein strength properties of tread improves. Tread rubber wearability increases, that, apparently, is caused by direct interaction functional group, located on the surface of zeolite with rubber to structure formation of elastomer matrix.

Thus, employment of natural zeolites of Chankanaiski deposit not only improves physico-mechanical properties of tyre rubbers, and considerably decreases ecological pressure on the environment.

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KINETICS AND MECHANISM OF POLYMERS IMIDIZED POLYIMIDE PRECURSOR IN THE SOLID PHASE IN THE PRESENCE OF ORGANOSILICON COMPOUNDS

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The disadvantage of the existing industrial technology of producing polyimide (PI) film by thermal imidization of polyamic acid (PAA) is a large energy costs associated with high temperature and big duration the process. In order to find an alternative preparation method of PI film, we suggested idea of thermochemical imidization of polymer precursors- PAA and PAA trimethylsilyl ester (PASE) in the presence of alkoxy-substituted organosilicon compounds (ASC) as cyclization agents at moderate temperatures (100–140°C). PAA and PASE films with a thickness 5–20 μm cast on a glass substrate and dried in air at 60°C were treated with ACS at 100–160°C. Imidization kinetics was followed by the method IR-spectroscopy using peaks at 1340-1400 cm^{-1} (N-C val. imide. cycle) and 1500 cm^{-1} (C-C val. arom.).

At 140°C, about 70% imidization conversion is achieved in 25 minutes but stops growing furter. Addition of a tertiary amine leads to an increase in imidization rate and the final conversion up to 80%, however, but the process stops again. Mechanical properties of films with 70 and 80% conversion are rather poor compared with that of initial prepolymers. To elucidate the mechanism of this phenomenon, the model reaction was studied of phthalanilic acid trimetylsilyl ester (TMSPA) with trimethylsilanol (TMS), ethanol and water using 1H NMR method in $CDCL_3$. It was found that TMS as well as ethanol and water, reacts easily with TMSPA to form phthalanilic acid. So, it can be concluded that PASE moieties extremely unstable with respect to the low molecular weight products released on its imidization and transforms into PAA moieties. In turn, PAA moieties which are the thermodynamically unstable at these conditions and dissociate with formation of amino- and anhydride groups. This leads to decrease in molecular weight and poor mechanics of the samples and incomplete imidization process.

STUDY MOLDING PROCESS SYNTHETIC YARNS COMPRISING METAL NANOPARTICLES STABILIZED POLYETHYLENE

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Rapid technological progress at the end of the 20th century demands new textile materials. They should possess specific qualities which are necessary for a certain sphere of man's activity. Textile materials with such qualities are named the so called "intelligent" textiles and they are widely used for military and space industry. Mountain-climbers, sportsmen and sportswoman, people working in extreme conditions use clothes made of those textile materials. The main aim is to create the materials which have the properties such as: antibacterial qualities electroconductivity and fine physico-mechanical characteristics.

The synthetic yarns get useful qualities by introducing the metal nanoparticles into a polymer melt. Nowadays this method is the most perspective and economically-grounded. It does not require essential changes of technological conditions and the use of additional modified equipment. The following equipment was used for studying the formation process and orientation exhaustion: CFPB-1 and OCB-1 test benches. Thanks to this equipment it is possible to create the synthetic yarns with new qualities and perfect the technology of their production.

The purpose of this work was to study the influence of the formation parameters on physical-mechanical characteristics of polypropylene yarns with nanoparticles of metals.

It was necessary to choose a required nanoparticles of metals quantity which provides necessary quality of polypropylene yarns.

Metal nanoparticles were administered in form of polypropylene fibers in a polymer based on polyethylene concentrate.

Polypropylene yarns were formed on CFPB-1 test bench. The temperature of formation in working areas was: T1 equals 130 (degrees centigrade) (preheating zone), T2 equals 220 (melting zone), T3 equals 220 (stabilization zone), T4 equals 220 (heating zone of a formed plate). The speed of the forming disks was 100 meters per minute and was defined by technological reasons and constructional peculiarities of the test bench. These parameters remained constant during the experiment.

The nanoparticles of iron, nickel, cobalt and manganese, the stabilized polyethylene, the present work were used at the present work.

The concentration of nanoparticles in the polypropylene filaments is 0.1 - 1%. Influence of metal nanoparticles on the physical and mechanical properties of polypropylene yarn, biocidal and their electrical resistance.

This study was financially supported by the Russian Foundation for Basic Research (project No. 13-03-12065-ofi-m).

THE USE OF BIODEGRADABLE POLYMERIC HYDROGELS IN DURABLE ACTION ANTISEPTIC DRESSINGS

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Lately in biomedicine developments of drugs with controllable release arouse growing interest. This relates not only to finished dosage forms but also to creation of wound dressings having synergistic therapeutic action. Ones of the most prospective are dressings containing immobilized enzymes and antimicrobial or other drug substances. An example of such dressings can become polymeric hydrogels.

The polymeric hydrogels represent cross-linked hydrophilic polymers able to absorb large quantities of water.

Available now polymeric hydrogels almost exclusively represent goods based on acrylic polymers, and, so, are not biodegradable.

In the given work polymeric gels obtained from a mixture of hydrophilic polymers (polysaccharides) – carboxymethylcellulose and hydroxyethylcellulose and a bifunctional linking agent – citric acid were used. The latter gives the cross-links which guarantee the structural integrity of polymer-liquid system and promotes the retention of a water phase inside a molecular mesh.

Formation of cross-links were carried out at temperature of 90^0C during 20 hours. Swelling ration (SR) of the obtained polymer hydrogels was about 20, where SR is a measure of capacity of polymeric hydrogel to absorb water and is a ratio of absorbed water amount to hydrogel mass before absorbing.

At a stage of mixing in reagents into the gel structure such compounds as benzalkonium chloride (BC) and octenidine dihydrochloride (ODC) in number of 0,1 wt. % were added. The given compounds have pluripotential antimicrobial properties at low toxicity.

An investigation purpose was determination of a level of release of active components from polymeric hydrogel in time at room temperature during water absorbing by the gel.

An amount of BC and ODC was determined using a method of high-performance liquid chromatography from calibration curves made before.

The obtained data showed that after 24 hours of swelling an amount of released BC and ODC containing in a hydrogel reached 75% and 65%, respectively. A main release of bactericides is observed within first 2-4 hours (up to 60% and 55%, respectively).

The obtained capacity of polymeric gels under study to release a large amount of an active drug substance at a first stage of swelling allows quickly attain the bactericide action in respect of a broad spectrum of bacteria and can be used for infected wound healing. When contacting with wounds such dressings are able to absorb the excess secretion with simultaneous releasing active drug substance, at insufficient moisture – to moisten a wound maintaining its hydrobalance and ensuring the most favorable conditions for wound healing and epithelium advancing.

ANTICANCER DRUG LOADED NANOGELS: SYNTHESIS AND CHARACTERIZATION

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Selective delivery of drugs and diagnostic agents in the body is the focus of many research groups in the world. One of the promising nanocontainers is nanogel – soft nanoparticles, consisting of hydrophilic or amphiphilic polymeric chains. Nanogels have beneficial characteristics: high loading capacity, stability and sensitivity to environmental changes (pH, ionic strength and temperature). The aim of this study was to synthesize the nanogels and to analyze the loading and release kinetic of anticancer drug Dioxadet.

Nanogels were synthesized from block-copolymer polyethylene glycol-*b*-polymethacrilic acid (PEG-b-PMAA). Synthesis consists of several steps: 1) formation of polymer polyelectrolyte complexes with oposetly charged ions (e.g. Ca^{2+}); 2) cross-linking of formed nanoparticles by ethylenediamine using carbodiimide; 3) removing Ca^{2+} ions from nanoparticles through chelating with EDTA and thorough dialysis. Loading of drug into nanogels was processed by their mixing at different molar ratios and pH (25ºC, 10h). Loaded nanogels were purified by multiple centrifugation on Amicon filters (MWCO 30 kDa). Loading capacity was calculated with help of spectrophotometric analysis. Release of drug was studied at different pH and temperature.

Stable negatevly charged nanogels with cross-linked core were synthesized and characterized. Using DLS method we found that size and ζ-potential of nanogel changed during drug loading. Loading capacity of nanogels was strongly dependent on the ambient pH during the process (max loading capacity was at pH7 – 45%). We found the optimal pH and molar ratio drug/nanogel, wchich led to stable drug-loaded nanoparticles. The release of drugs was slow and slightly depended on pH as analyzed by dialysis method. Finally, the synthesized particles can be loaded with highly potent drug Dioxadet and exhibit sustained release of drug.

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PRODUCING OF ALKYD RESINS BY POLYETHELENE TEREPHTHALATE RECYCLING (PET)

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PET production in 2013 year was over than 20 million tons in the world and 425 thousand tons, while it's only 30% was recycled (160 thousand tons). The important feature of PET is that it's more easily recycling and homogenizing than other plastics. These features of recycled PET allowed him to become nowadays the most recyclable plastic in the world with a wide range of applications, ranging from granules and films for packaging, finishing garments, carpets, packaging tapes, printed and non-woven products, non-food bottles for liquids.

The purpose of this work is to develop new methods of PET recycling to alkyd resins, which are the basis for the production of varnishes for various functions.

The most well-known methods of PET recycling are:

- «mechanical» (75% of all recycled PET): this method is used for the production of packaging, fibers and yarns (sportswear, artificial fur, flooring), engineering plastics in the automotive and construction;
- «chemical» (5% of all recycled PET): is used for producing of polyesters in the production of adhesives, coatings, and raw materials for re-synthesis of PET;
- «thermic» (20–21% of all recycled PET): combustion for the heat energy or pyrolysis to produce liquid and gaseous fuels.

Due to the developed method, the recycling of PET is carried out by transesterification with glycerol in the presence of a catalyst of antimony trioxide, followed by polycondensation of oligomers obtained with phthalic or maleic anhydride, and with additives of oils also.

The experiments are designed compounding resins for the production of lacquers. These resins may be used for the production of coatings as thermal and air curing.

INVESTIGATION OF INFLUENCE OF EMULSIFIER CONCENTRATION ON THE PROPERTIES OF THE AQUEOUS PHASE FOR BITUMINOUS EMULSIONS

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The most common type of organic binding materials today is petroleum bitumen. Due to the limited reserves of oil and raw materials needs of large road construction materials in organic binders particularly urgent expansion of resources to get them through the use of various industrial wastes, as well as the development of technologies to produce efficient and environmentally friendly organic binders and road-building materials based on them.

One of the effective areas of materials science in the road, allowing a comprehensive approach to solving the actual problems of the industry such as resource-and energy-saving, environmentally friendly technology and manufacturing process, as well as an extension of the construction season to improving the quality of road surfaces is the development and introduction of bitumen-emulsion technology.

Known for a large number of domestic and foreign works, aimed at studying the processes occurring at the stage of preparation and the structure of the final product - bitumen emulsion, which contributes to the complication, elongation, and emulsion manufacturing costs through the issuance of a large number of test pilot batches of bitumen emulsion- the step of matching and adjustment.

In the present study revealed the nature of change dependencies performance properties, dispersion and stability of bitumen emulsions on the concentration of emulsifier in the composition of an aqueous phase is to improve these indicators using rational emulsifier concentrations due to the formation of different amounts of surfactant molecules electric layers at the interface.

The correlation between the surface tension of the aqueous phase and the decay rate of the final bitumen emulsion that will predict and regulate class decay rate of the final product at the stage of its preparation.

The dependences of the surface tension and contact angle of the aqueous phase, the concentration of emulsifier in its composition having a saw-tooth profile. Revealed that in the range recommended by the manufacturer of the emulsifier content in bitumen emulsion, there is not effective concentrations, whose action and variability seen in contact with mineral materials of different nature.

The necessity of a detailed study of the aqueous phase for bitumen emulsion emulsifier concentration in its composition, as well as compatibility with a specific mineral material used in production.

Proposed a method for adjusting the formulation of bituminous emulsions, which can accelerate the process of transition from laboratory selection of the industrial production of the finished product with the desired properties, allowing them to reduce labor costs and reduce material and energy consumption of the process.

The article presents the results of the work performed within the public task of the Ministry of Education and Science of the Russian Federation № 1950, as well as of the strategic development program BSTU. VG Shukhov for 2012–2016.

EFFECTIVE NANOMODIFIED ORGANIC BINDERS AND COMPOSITES BASED ON THEM FOR THE CONSTRUCTION INDUSTRY

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In 2008, the program of the nanotechnology development has been adopted in Russian Federation until 2015. The main objective of this program is to form a Russian nanotechnology industry sector, capable of competing with the most economically developed countries in the world in all areas that affect the technological and economic security for defense capability of Russia, as well as the quality of life of its population.

The key point in determining the quality and life of the population dynamics is a country's transport infrastructure, the efficiency of the establishment and operation of it, in some aspects forms the road construction industry For it, the perspective direction of improvement a quality of construction designs and compositions, is to use the methods of nanomodification.

Therefore, in the present work were considered modify nano-objects: single-walled and multi-walled carbon nanotubes (OUNT and MUNT), and also a number of methods of nanomodifying the organic binders: preliminary preparation nanomodified precursor and subsequent introduction into the bitumen, the second - by sequential mixing of the components. It has been established and confirmed experimentally directed regulation properties of organic binders using nanoscale objects, allowing to receive the binder for road construction industry with properties, significantly exceeding the required performance is not only about existing regulations, but also with a significant reserve of performance and physical and mechanical characteristics. Such as elasticity, adhesion and cohesive strength, temperature sensitivity, etc. for specific conditions.

Based on the developed polymer-bitumen compositions modified nanoscale objects were prepared for various organic-track road industry: mastics, sealants and asphalt mixture. Established that using of nanomodified binder in preparation technology road tracks significantly changes their performance and durability properties. To explain the processes occurring during nanomodifying organic binders was an attempt to "look deeper into the processes." In the theory of macromolecular organic binders are presented as solutions of different form chains of macromolecules. According to this, the bitumen – the high polymer material composed of branched molecules with ring links, interconnected representing the totality of oils, resins and asphaltenes.

To exploration asphaltenes given increased attention from the petrochemical gas, and in the road sector this one are poorly understood, although make essential impact on the structure of bitumen. A number of responses to emerging issues in the study was obtained by studying the effect of nanoscale objects on the structure of asphaltenes in the bitumen, bitumen nanomodified relationship properties and their structures, processes and aggregation of asphaltene peptization of the bitumen under the influence of nano-objects.

Despite the fact that nanotechnology are complex and expensive areas of research, it should not decelerate their evolution because simple technology in many industries are often have exhausted themselves.

COLLOXYLIN FROM OAT HUSKS

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In connection with the search for new cellulose sources for the manufacture of colloxylin called-for in medicine, building industry, and precision machinery industry, the chemists have intensified their studies and put herbaceous plants [1, 2] and bacterial cellulose on the list of potential raw materials. But there are no examples of producing cellulose nitrates (CN) with colloxylin properties from industrial crop processing waste, particularly from oat husks.

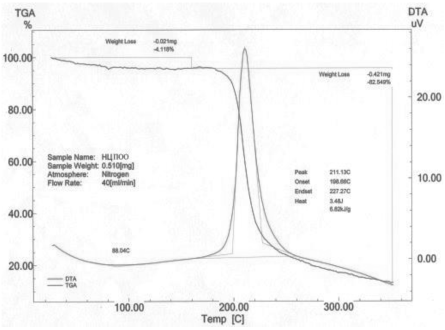

Fig. 1. DSC of oat husk CN.

Oat husks are known to be an industrial source of xylite because of the high content of hemicelluloses, irrespective of where grain-processing plants are located. However, there is a lack of implementations of schemes for chemical conversion of oat husks into useful products. In view of the acute need to resolve the problem with disposal of growing oat processing residues (cellulose content in oat husks is 35-40%), priority research has been performed at IPCET SB RAS to develop methods for producing high-quality cellulose from oat husks with subsequent synthesis of cellulose nitrate having colloxylin properties. It is worth noting that additional efforts were needed in order to ensure purity and chemical stability of oat husk colloxylin.

Figure 1 illustrates differential scanning calorimetry (DSC) results of an enlarged sample of oat husk cellulose nitrate as a confirmation that the problem raised has been resolved. The presence of a narrow exothermic peak and high onset temperature of decomposition indicate that the product is free of impurities that promote self-decomposition of the product over an extended shelf life. Supplementary studies of the oat husk colloxylin by the ampule-chromatographic method have corroborated the sufficient chemical stability of the new product [4].

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POLYMER NANOCOMPOSITE MATERIALS FOR AUTONOMOUS ENERGY SOURCES ON THE BASIS OF FUELS CONVERSION

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Development and creation of autonomous energy sources (AES) on the basis of high-efficiency fuels conversion are fundamental scientific problems of modern power engineering and nanotechnology. One of the main lines of catalytically active, stable and cheap catalysts development for AES of new generation is the inclusion of nanostructured metals into functional matrices. At present time the most relevant and promising energy sources are fuel cells with solid polymer electrolyte (FCSPM) due to their extensive use in stationary applications and mobile electronic equipment. Electrolyte in such FCSPM is proton exchange perfluorinated polymer with ionogenic sulfo groups ($–SO_3H$) of the Nafion type (Du Pont) that provides unipolar conductivity on hydrogen ions [1–3].

As nanostructured matrix-substrate in our work it was used the Nafion type solid polymer membrane (SPM) with a thickness of less than 0.2 mm. The modification by one-component and bimetallic nanoparticles of platinum and base metal of the SPM surface and volume promotes additional catalytic oxidation of hydrogen-containing fuels (H_2, C_2H_5OH, HCOOH, CH_3OH and others). Due to introduction of nano-sized metal in the polymer matrix and application of «core-shell» systems there is an increasing of the catalytic and functional activity of metal-polymer nanocomposites and reduced the consumption of expensive Pt and Pd catalysts [1, 2].

The purpose of research is creation of high active and stable nano-membrane materials for efficient conversion of fuels-reducing agents for autonomous energy sources of new generation with high operating characteristics.

Synthesis of polymer nanocomposites was carried out by γ-irradiation ^{60}Co reduction of platinum metal ions in water-organic solutions of reverse micelles [2]. By varying the synthesis conditions one can control the nanoparticles size, content and emerging properties. By means of the modern physico-chemical research methods, as electron microscopy, x-ray phase analysis, cyclic voltammetry it was performed the investigation of nanoparticle and nanocomposite functional properties. It was found that when reducing the size of metal nanoparticles (less than 8 nm) catalytic activity of metal/polymer nanocomposites (current density, catalytically active surface area) increases [2].

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MOLECULAR WEIGHT INFLUENCE ON THE SLIP EFFECT

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There is a number of technological problems associated with the deformation and melt flow during the processing of polymers and polymer composite materials (PCM).

In the polymeric materials composition has entered different nature and compatibility rheological additives that is greases, lubricants, etc, to improve the processability and viscosity regulating properties. Most rheological additives employed by sliding effect stand on the surface of the polymer melt and form a thin layer of low molecular weight substances . To form such low molecular weight substances layer is important both thermodynamic compatibility of additives with the polymer melt and the molecular weight of the additive. Investigation of sliding effect parameter dependencies from the molecular weight characteristics of polymers and rheological additives is an important task in polymer and PCM processing technology.

The paper gives details of the slip effect study by compositions on the basis of a low density polyethylene LDPE 10803-020 (MFR = 2,0 ± 10 g/10 min) and polyethylene company SABIC HDPE M500026 (MFR = 50 g/10 min).

The compositions was produced by laboratory rollers under optimal mixing conditions. Rheological properties of polyethylene compositions with different molecular weight were examined by the method developed at the Department of CTPP and PCM in MITHT named after M.V. Lomonosov, on capillary viscometer Dynisco LCR 7100 with different diameters and lengths capillaries at 190ºC. The main wall slip effect indicators were chosen: wall slip velocity at a given shear stress on the wall of the capillary, sliding flow volume.

It is shown that both types of polyethylene with different molecular weights show sliding effect. Displaying a fluent slip velocity increases after adding a polymer with a low molecular weight capillary. Was illustrated division of polymer melt expense from viscometer due into two parts: flow ensured by sliding and ensured by bulk flow. It is shown that with increasing concentration of polyethylene with a lower molecular weight fraction increases flow amount provided by the slip and the concentration after 60 pph can reach a regime in which the flow of polymeric material from the capillary is performed almost completely by sliding

Thus, on the basis of rheological additives efficiency assessment methodology developed at the department of CTPP and PCM in MITHT named after M.V. Lomonosov was studied parameters depending the molecular weight of the polymer on wall slip.

ANTISTATIC POLYURETHANE COATINGS WITH ADVANCED PHYSICAL AND MECHANICAL PROPERTIES

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By using of highly ordered coordination compounds of transition metals was obtained antistatic polyurethane coatings . This coating has the ability to efficiently remove the static electricity, adhesion to various types of surfaces, high resistance to solvents, alkalis, acids, and water, high weathering resistance, low gas permeability, a high resistance to abrasion and ability to maintain the stated performance and consumer properties over a prolonged period time.

Currently, the various branches of industry use a variety of protective coatings to protect the internal surfaces of chemical reactors and oil pipelines. One important drawback of this protective coatings is their inability to discharge static electricity, lack of resistance to various corrosive environments, low resistance to hydrocarbon solvents, mineral oils, high cost of the initial reactants and the complex technology of producing and applying this coatings.

This approach is based on the use of highly ordered transition metal coordination compounds with the aim of creating conductive structures in a protective coatings. Using this metal complexes allows to obtain different coatings with antistatic properties, improve physical and mechanical properties.

Properties of this coatings presented in the table:

Property	Value
Adhesion (GOST 15140-78)	no more than 1 point
Swelling in - water - white-spirit - mineral oil	 <0.5 <1 <1
Tensile	35-45 MPa
tensile elongation	30-50%
thermal spalling resistance	>250 ^{o}C
drying time	0.15 hours
Pot-life	3-4 hours
curing temperature	20-30 ^{o}C
modulus of elongation, E(b)	300-400 MPa
volume resistivity	<10^{10} Ohm*cm

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Section 6

Solutions of Ecological and Economic Problems in Chemical Engineering

SORPTION OF ZINC, CADMIUM AND LEAD IONS BY CATIONITES WITH VARIOUS FUNCTIONAL GROUPS

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When developing sorption technology of extraction of this or that element one of the main tasks was approbation and choice of the sorbent with high capacity and selectivity in relation to the aimed element. Equilibrium and kinetic characteristics of sorption of studied ions by cationites with various functional groups (Amberlite IRP-64, IRP-69, IRC-748 and Diaion CR-11) are estimated. It is shown that sorption efficiency depends on pH of processed solution – at pH < 2 degree of sorption of the studied ions sharply decreases owing to a competing sorption of hydrogen ions. At the pH values, close to pH of hydration of concrete metal, access of metal ions to functional groups is complicated because of formation of hydroxo-complexes.

Sorption isotherms in the field of concentration from 0,25 to 2,50 g/l are investigated. Dependence of $E = f\ (C_t)$ looked like the Langmuir isotherm for all studied systems. Parameters of the Freundlich equation are also calculated and corresponding equations are offered. The maximum values of exchange capacity, marginal coefficients of distribution and K_{exch} are calculated from isotherms. Along with equilibrium characteristics of absorption of metal ions by cationites kinetic parameters of sorption are obtained. Diffusion coefficients of ions in cationites with various granules in solutions of various concentrations are calculated. The mechanism of the studied processes corresponding to internal diffusion kinetics is revealed by means of the calculated Bio criteria. It is ascertained that at the same concentration sorption speed of the studied ions is so higher than more selective is the cationite to the incoming ion. Values of effective diffusion coefficients for the studied ions increase with increase in concentration of external solution. Diffusion coefficients of cadmium ions in the ion exchanger of Amberlite IRC-748 are much lower than the corresponding values for zinc and lead ions and make $2{,}4.10^{-8}$ and $2{,}75.10^{-8}$ cm^2/sec. that provides higher absorption degree of zinc and lead ions by the cationite.

On IR-spectra of the studied ionic forms of cationites there is a wide absorption band of the difficult configuration in the field of 3700–3000 cm^{-1}, consisting of several maxima, their situation and intensity depend on properties of retained cations. On IR-spectra of the studied ionic forms of cationites there are narrow, but well expressed maxima at about 3700 cm^{-1} caused by fluctuations of free OH-groups of water which intensity depends on humidity of cationites. At realization of aqua-complexes with octahedral structure there are maxima in the field of 3200-3100 cm^{-1} on their spectra, caused by fluctuations of water molecules located in tops of octahedron. For tetrahedral structure absorption at 3350–3300 cm^{-1}is more characteristic, it is caused by fluctuations of water molecules located in the tetrahedron plane. Verification of the technological scheme of sorption extraction of zinc, cadmium and lead from production solutions in laboratory scale has shown high efficiency of processes of purification of solutions from the studied ions up to sanitary standards and production of the corresponding compounds of zinc, cadmium and lead of “pure” brand. Results of the work carried out give the chance to recommend the carboxyl cationite of Amberlite IRP-64 for sorption of the listed ions from rinsing waters and possibility of creation of the closed water cycle.

ELIMINATION OF OIL SPILLS BY APPLICATION BIOLOGICAL MATERIALS A BIOLOGICAL PRODUCT «NEFTEDESTRUKTOR»

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Oil production, transport and processing are often connected with leakage of hydrocarbons, that leads to deterioration of an ecological situation. The technical devices aren't capable to provide full cleaning pollution of objects. Cleaning territories from oil and oil products solutions can biological resource. Biological methods of cleaning water and soil from oil and oil products it is reduced to use microorganisms – oil destructors [1–3].

At the first stage of researches was studied ability of natural microflora to acquire oil and oil products. For this purpose soil samples took from places which polluted by oil and oil products long time. Samples took from territories of garages, fuelling stations and oilfields areas Mangyshlak and Tyub-Karagan.

Experiments were made on 2% agar environment with an additive of sources of mineral saturate. In series of experiments was studied activity of soil petro acquiring microorganisms, concerning various fractions of oil. For comparison took hydrocarbon appropriate type of yeast of the sort «Candida».

At the first stages was established that the soil in territories of fields Tomsk and Tyumen areas contains the microorganisms acquiring oil. There is enough to introduction of mineral additives for stimulation of their activity. For check of these conclusions experiment was made in oilfield conditions. For this purpose the site of oil spill was processed by mix of mineral additives.

Experiments in comparison of efficiency of weeding from oil were in vitro made at various options of processing. Various options of processing were studied. Initial level of pollution by oil made 5%. It was established that in 15 days the content of oil considerably decreased.

Experiences showed that introduction of bioadditives considerably accelerate oil destruction. The received results were checked in oilfield conditions. Zhetybay oilfield ares was processed in 2013. The age of oil spill was made by 1 year, the soil argillo-arenaceous. Level of pollution is 14 – 30% of oil in a waterless sample. Results were received during 70 days.

Thereby, it was shown that in real oilfield conditions the good effect gives to use as «Candida» yeast, and soil culture. However for ensuring ecological purity at work in extensive territories, it is obvious, expedient to use soil culture. As, those species of microorganisms which are usual for cleared territories are thus used. Use of such types liquidates risk of unpredictable ecological consequences which are possible when using «Candida» yeast or active silt. Advantage of soil culture is also ability to grow it in oil weight, and not just on limit of the section. Besides, such culture is effective and concerning high-sulphurous oil of the Karazhanbas oilfield.

Results of researches allow solving large-scale ecological problems of water purification and soils from oil and oil products. The way is effective on all levels of production. That is, at oil production, oil transport, processing and products sale. For one season level of pollution decreases by 10 – 100 times.

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METHOD FOR PRODUCING ELASTOMERIC COMPOSITES REZINOTEHNICHESKIE APPOINTMENTS

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Currently developing rapidly on the basis of production of recycled plastics, which is characterized by unprecedented growth, stimulated by the needs to reduce the cost of manufacture, they saturate the market and comply with increasingly stringent environmental legislation. Development and implementation of low-and non-waste technologies − this is one of the most effective and promising way to reduce the proportion of waste per unit of output. In some countries, this method of reducing the amount of waste is seen as strategic, aiming simultaneously to the rational use of natural resources and environmental protection. However, no production without any waste is fundamentally impossible. In connection with the foregoing, it is urgent to develop a method of manufacture of elastomeric composites rubber- destination, where all raw materials and energy are used efficiently and comprehensively as possible.

The aim of this work was to develop process of manufacturing rubber products using waste rubber industries.

The solution of the goal − it is more convenient process than the collection, removal and disposal.

Our studies have shown that the production of a composite material using the composition of waste in its production of rubber (crumb rubber and reclaimed) justified technological and economic points of view. The resulting compositions exhibit a good combination of strength and performance conditional elongation , hardness and friability. This is probably due to the fact that the elastomeric composite material containing in its composition along with the rubber recycled materials has a sufficiently dense spatial mesh, which positively affects the physical and mechanical characteristics. Also important is the fact that the cure time is reduced by 5–7%, it indicates that the proposed manufacturing method is energy-efficient process, and the economical use of the electric energy helps to conserve natural resources and reduce the cost of the finished product.

SYNTHESIS OF GAS-LIQUID POLYCONDENSATION FIBRID: ECOLOGY AND SAFETY OF PRODUCTION

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One method of producing synthetic fibrides – precipitation of the polymer from the solution in the hydrodynamic field vysaditelnoy bath [1]. Production includes five main stages: preparation of the reaction syrup (concentration of the polymer in dimethylacetamide 10–12%); preparation of the spin bath; precipitation of fibrides and washing fibrides; solvent recovery and bath for precipitation. Flow rate of the solvent in this process is 9 tons, precipitation bath – 60–70 tons, water for wash – 200–250 tons per ton of polymer.

Designed in Tver State Technical University reaction molding method of polyamide fibrides GLC polycondensation (GZHPK) [2] is characterized by high environmental and waste-free and consists of two main processing steps: 1) the reaction of polyamide molding fibrides gas-liquid polycondensation; 2) washing, spinning and packing of the product.

The process differs ecological purity: solvents and precipitating agents are not used in the production of organic, flammability hazards and production, the carrier of the monomer gas phase is air. Construction of the reaction chamber of reactor-fibridator [2] at steady state operation eliminates leakage of the gas phase, which provides protection of the air pool as emits only air with traces of non-condensed water vapor. In addition to structural factors, the protection of the air basin provides a technological solution: the recommended molar ratio of monomers; defoamer mounted centrifugal separation step, followed by condensation of water vapor in the flue gas composition and demister after cooler. Possible replacement of inert carrier gas phase air condenses steam that completely eliminates the steam-gas emissions [3].

Watershed protection in the developed process is ensured organization two recycles: for the liquid phase (filtrate stage spinning polymer slurry) and the wash waters.

The filtrate containing the residues of a diamine and oligoamides soluble sodium chloride (NaCl), is continuously recycled to the liquid phase preparation of acylatable monomer (solution of diamine), except that the environmental effect saves fresh diamine.

The washing waters from the washing step is subjected to evaporation fibrids squeezed to remove excess NaCl and traces of the diamine, and flash steam is condensed and recycled to the return flushing fibrids, abruptly reducing the amount of fresh chemically cleaned water. Emitted during the evaporation NaCl (0,5 t / t fibrides) can be treated as a technical product in the production of chemical fibers.

Mounting foam extractor cascade-type between stages of separatoration of the reaction mass and filtering the slurry allows to extract excess diamine and water soluble oligoamides

PROSPECTS OF USING PLANT WASTE-BASED SORBENTS FOR DECONTAMINATING WASTEWATER FROM COPPER (II) IONS

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The most widely used cleaning methods in galvanic production are reagents or dolomite filters as a result of which the outgoing copper ion content corresponds to Cu^{2+} in a saturated solution of copper hydroxide at pH 7-8 0.1–0.15 µg/cm^3. The allowed standard concentration of copper ions for waters discharged into the municipal sewerage varies in different regions between 0.002 and 0.5 µg/cm^3. The use of sorption methods makes it possible to reduce the copper content in discharged waters to the standard amount. The farming production waste can be used as a raw material for producing sorbents which solves such ecological problems as recycling of vegetal waste and cleaning of effluents.

PU-1, PU-2, and PU-3 sorbents (Table) were derived from farming production waste while AN-K4 activated coal was obtained from anthracite by a method developed at the Moscow-based M.V. Lomonosov State Academy of Fine Chemical Technology [1].

Physical and chemical properties of sorbents under study

Sorbent	Specific surface, m^2/g	Total alkalinity, mmol-eq/g
PU-1	130-150	2.24
PU-2	160-180	4.64
PU-3	250-300	2.70
AN-K4	≈1,000	1.87

The total alkalinity of sorbents was determined based on results of the reversal acid-base titration. The sorption was studied in static conditions at the ratio sorbent: reference solution 1:1,000 in the range of copper ion concentration ($0,4\cdot10^{-3}$ mmol/l to 0.08 mmol/l), exposure time 24 hours, Cu^{2+} content in solutions before and after sorption was determined by extraction and photometric measurement of lead diethyldithiocarbamate.

Dependence of the sorption extent on the pH was investigated in the pH range of 2 to 8, in which case the initial copper concentration in solution was 1 µg/cm^3. It was determined that in the pH 2-3 range the Cu^{2+} ions are practically unextractable from the solution; in the pH range of 4 to 7 a gradual growth is observed in the absorption extent while at pH 7-8 the maximum sorption takes place. Sorption isotherms were built at the optimum pH. The obtained isotherms are of the H type which testifies to the strong interaction of the extracted component and the sorbent. At the low concentration (up to 1 mg/l) the copper cations are extracted from solutions by sorption processes. At the higher concentrations the Cu^{2+} ions are extracted from the solution through deposition by formation of hardly soluble copper hydroxide and bicarbonate on the sorbent surface and as a suspension which is determined by the significant alkalinity of PU sorbents. The maximum extraction at low concentrations is characteristic of PU-1 sorbents (72-99%) and AN-K4 (62-90%) which can be regarded as the most promising for sorption-based water purification.

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STUDY OF SUBLIMATION OF BINARY MIXTURES OF RUBBER ACCELERATORS

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Organic accelerators of sulfur vulcanization of rubbers are molecular crystals. When mixed and heated these accelerators, can be prepared a eutectic mixture or solid solution substitutions. Binary eutectics have the property of granulation. This indicator is important for greening technologies on preparatory production.

In this regard, we have conducted researchs for binary systems accelerators. As such as: tetramethylthiuram disulfide (TMTD) – 2 benztiazolilsulfenamid (CBS), benzothiazole, 2,2-dithiobis- (DBTD) – TMTD, 2-mercaptobenzothiazole (MBT) – TMTD.

The results showed that granulation of these systems accelerators in rubber compounds may be in proportions corresponding to the interval between two eutectic melting temperatures. At a temperature of 111°C [1], on the phase diagram of a binary mixture have characterized by the formation of eutectic. This indicates the formation of a eutectic melt of new chemical compounds.

Based on studies sublimation vulcanization accelerators rubber compounds, we can propose the following ways to reduce their emissions during storage and transport [2]:

- preparation the mechanical of mixtures of accelerators and zinc oxide in the desired ratios;
- preparation fusible and solid granules obtained from eutectic melts of binary mixtures of ingredients. At that this sublimation occurs only from the surface of the granules;
- transportation and storage of the last in a sealed container in view of the saturated vapor pressure accelerators.

As a result, the above method can substantially reduce adverse effects. These adverse events may lead to contamination of the environment due to the emission of highly toxic sulfur vulcanization accelerators rubbers.

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THE METHOD OF DEALING WITH THE WASTES OF AMMONIUM NITRATE PHOSPHATE FERTILIZER PRODUCTION

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Large quantity of the precipitated calcium carbonate, minor part of which is used in building materials and agriculture, is produced as a co-product in the factories of the chemical industry while ammonium nitrate phosphate fertilizer production. The rest part of it is stockpiled.

The process chalk has the following composition: calcium carbonate – 90.5%; the substances that are insoluble in the hydrochloric acid – 0.47 %; water-soluble substances – 0.650 %; water – 0. %; ammonium nitrate – 0.3 %. Poured density is 1,301 gram per cubic centimeter; sieve № 0045 residue is less than 0.1%.

We suggest that after additional treatment (drying, screen fines, grinding) and hydrophobization, precipitated calcium carbonate can be used as the filler for production of the highly-filled elastomeric compositions.

To increase dispersity of the filler precipitated calcium carbonate should be grinned in the ball mill together with the hydrophobisator – stearic acid, which is a dispersing and plasticizing agent in the rubber compound. 95% of the obtained filler consists of the particles the size of which is less than 10 micron.

Elastomeric compositions are made by the method of liquid-phase filling at the latex stage. This allows putting into practice low power-consuming superposition and homogeneous distribution of the filler over the polymer master. The quantity of the carbonate filler may vary between 100 and 400 pts. wt., while the quantity of the polymer is 100 pts. wt.

Depending on the application field (linoleum production, production of rubber, building mix additive, a component of the road marking or roadway covering stuff), elastomeric composition may have the structure of powder, granule or entire fragment.

Thus, using elastomeric compositions based on precipitated calcium carbonate may cut production costs and solve the problem of the wastes use.

RECONSTRUCTION PROBLEMS OF ENVIRONMENTAL STRUCTURES IN THE UNINTERRUPTED OPERATION

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Lifespan of most industrial enterprises to date exceeds 50 years, technological schemes do not meet the standards of industrial and environmental safety, and require extensive renovation of production as the main technological cycle and environmental protection facilities. Only in the Samara area more than 60% of industrial enterprises are currently under active reconstruction and modernization. Moreover, more than half of them are the petrochemical complex and their activity is accompanied by the formation of liquid and tabular waste .

Common method of neutralization of waste generated to date is their location and storage in specially equipped facilities (oil separators, storage, buffer ponds, etc.). Increasing of environmental regulations pressure, changes in the basic approaches to the processes of maximum use of secondary raw materials (including on the basis of waste) determines the need for a fundamental reconstruction of environmental facilities. Due to lack of free territories the creation of modern multifunctional complexes of raw materials recycling and recycled materials production on the basis of existing enterprises seems to be the promising direction of reconstruction.

The main purpose of the development of this sector in the context of large industrial agglomerations is the development of fundamental structural and layout diagrams of recycling systems for renovation of environmental protection facilities.

Achieving this goal involves the following problems:

- Selection of the main functional parameters and structural and technological features of the object for its assessment as the site for complex recycling;
- Identification and classification of the limiting factors on the intended direction of the reconstruction;
- Development of design-layout scheme of reconstruction of the object in the chosen direction;
- Assessment of the main types and levels of environmental impact during the reconstruction of the object and after its completion;
- The use of the territories after reconstruction for future development.

The report represents a detailed technical justification of fundamental structural and layout schemes of complex recycling, and technical and economic assessment of the costs in terms of environmental facilities for advanced treatment of biochemical oily waste at one of the petrochemical complexes of the Samara region.

SOLVENT FREE TECHNOLOGY FOR SILICONES PRODUCTION

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Silicones have a number of unique features, which are absent in any other known substances: the ability to increase or decrease the adhesion, to give hydrophobicity, to work and to save the properties under extreme and rapidly changing temperatures or high humidity, moreover, silicones have good dielectric properties, chemical inertness, elasticity and durability. Thus, silicones are widely used in industry.

The hydrolytic polycondensation of organochlorosilanes is the main method of silicones producing. Hydrolysis of such highly reactive monomers requires the use of large amounts of organic solvents and water, hydrolysis is followed by hydrogen chloride, which leads to rapid corrosion of equipment and production facilities, formation of acid wastewater fouleds by silicones, solid salt residues. Recycling of hydrogen chloride by stripping or chemical bonding does not solve this problem.

Substitution organochlorosilanes by organoalkoxysilanes can significantly reduce environmental hazards, because the hydrolysis of such monomers results in alcohol which can be easily recycled and returned to production.

However, this is only a partial solution, as today organic solvents are used in the hydrolysis of organoalkoxysilanes.

The usage of solvents in the hydrolysis of various monomers is caused by many variables. The solvent is designed to dissolve the starting monomers as well as formed polymers and to reduce side processes, it is also can be used for the removal of low molecular products, etc. In the hydrolysis of organochlorosilanes a solvent is a regulator of the water/monomer ratio in the reaction zone. Such regulation is possible in the kinetic regime of the process. We found that the kinetic regime is easily achieved when reactive organochlorosilanes is replacemed with less reactive organoalkoxysilanes.

It is established that the composition of products depends on water/alkoxysilane ratio. The selection of method of synthesis (solvent free or in miscible or water-immiscible solvents (ketones, nitriles, ethers, esters, alkanes, and aromatic hydrocarbons)) does not affect the composition of hydrolysis products. This fact obviously points to the kinetic regime of the process. Water delivery into the reaction zone is provided by an increase its solubility in this region due to the formation of hydrophilic molecules of organohydroxyalkoxysilanes, by alcohol homogenization, and by the fact that the diffusion of water keeps pace with the reaction. This "feeding" of reaction phase is used by LLC "SPF" MIKS" in the solvent free technology production of silicone varnishes and resins of branched, cross array and spirocyclic structures.

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A SULPHUREOUS WASTE PRODUCTS: NEW METHODS OF THEIR UTULIZATION

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Sulphureous wastes are byproducts of increasing volumes of sulfur-containing hydrocarbon feedstock. The problem of disposal of waste sulfur attributed to the increased environmental controls on the extractive and processing industries.

We propose new methods of disposal of waste sulfur due to the involvement of elemental sulfur and its compounds in the reaction polymers formation. One is the transfer of elemental sulfur in plastic, polymeric sulfur. Polymeric sulfur is not soluble in organic solvents, and rubbers can be widely used as a vulcanizing agent in the rubber and tire industries. Unlike conventional sulfur polymeric sulfur is not "fade" on the surface of rubber compounds, which allows to maintain the technological properties of semi-finished products for long periods of storage . Also, polymeric sulfur not able to migrate into adjacent layers of rubber multilayer systems provides more intense and uniform vulcanization while reducing the process time .

The second method for the disposal of sulfur is its use as a monomer in the synthesis of oligomeric sulfides. Polycondensation of elemental sulfur with substituted aromatic hydrocarbons synthesized new world oligo(phenylene sulfides) with - OH, $-NH_2$, $-CCl_3$ and others groups in the aromatic nucleus [1]. Such oligomers may be promising as components of systems for vulcanizing elastomers , and rubber articles such as tire rubber . Oligo(phenylene sulfides) this kind are of interest as components of stabilizing systems for most polymeric sulfur, preventing its depolymerization , which search is still an urgent task.

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ELECTRODIALYSIS FOR TREATMENT OF NITROGEN-CONTAINING SEWAGE FROM THE FACTORIES OF MINERAL FERTILIZER PRODUCTION

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When nitrogen-containing fertilizer is being produced, subsaline solution is generated in quantity. After demineralization it can be reused in the work cycle. Ammonium nitrate is the basic component of such water.To activate the process it is necessary to determine optimal current mode and rate limit. The experiment was carried out in the five section electrodialysiscell of the flowing type with the membranes MC-40 and MA-41.By electrodialysis of the waste waters the upper limit of ion flux is observed when the value of current density is 1,5mA/cm^2, which is the ultimate diffusive current density for the saline solution. When the current rises, ion flux decreases as there begins the transfer of the ions H$^+$ and OH$^-$ that are produced because of the irreversible water dissociation. This process causes excess demand energy but does not reduce salt concentration of the solution.

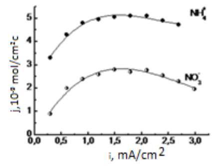

Fig. 1

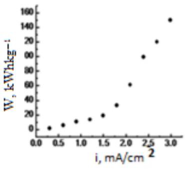

Fig. 2.

Fig. 1. The dependency of the ion NH$_4^+$flux through (MC-40) and the ion NO$_3^-$flow through (MA-41)on the current density.

Fig. 2. The dependency of the specific electricity on the current density during the waste waterelectrodialysis (the initial concentration of the ions NH$_4^+$and NO$_3^-$ is 8,2 and 3,7 mmol/l accordingly).

Fig. 1 represents ammonium ion and nitrate ion fluxexthrough the waste waterelectrodialysis. The ion NH$_4^+$ fluxis larger, because the initial concentration of these ions is more than the initial concentration of the nitrate ions. In the case of waste water,ion production at the limit condition on the membrane may lead to precipitation of the poorly soluble hydroxide on the anion-exchange membrane in the section of concentrating, as the stock solution contains the ions of calcium, copper and iron. The precipitate reduces the functional surface of the membrane, increases the electrical resistance of the cell, decreases current efficiency, and makes the further process impossible.The calculationof expenditure of energy (W) for production of one kilogram of ammonium nitrate through electrodialysis (Fig.2) shows that the quantity W increases sharply when the ultimate current density is exceeded.Note should be taken to the fact that the power inputs are given for a laboratory setup. Industrially the figures will be smaller because a multisectionalelectrodialyzeris used. We can draw a conclusion that during electrodialysis of the nitrogen-containing waste water of mineral fertilizer production dosing rate of the saline solution and the current should be chosen according to the current density which must be close to the ultimatediffusive density but not exceeding it.In this case the productivity of the cell has its maximum and additive processes, that prevent effective ion transfer, do not occur.

DOLOMITIC POWDER: AN INNOVATIVE ABSORBANT FOR THE LOCALITIES STORM WATER PURIFICATION FROM PETROLEUM PRODUCTS

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At the present time the quality problem of water resources is current for the Russian Federation and for the whole world in general. The purification of the oily localities storm water to the water reuse normative is a relevant objective nowadays. The valuation problem of the oily storm and melt waters pollution and also purifying methods for such waters are understudied as of now. The ingress of petroleum products to such waters is connected with leakage of fuel, motor oil, transmission gear oil, lubricating material and other chemicals of different systems.

As follows from the analysis of scientific and technical literature and patent research nowadays the most prospective oily water treatment methods include a processing stage to purify water with sorbents. In spite of the presence of different water treatment methods there are now methods for simultaneous purification of oily storm water and safe disposal of waste sorbent with the maximum use of it's resource potential.

Dolomitic powder is used as an absorbant in this experimental work. The main advantage of this material is that it can be used as an activated mineral powder after the enrichment with petroleum for the production of the bitumen-concrete mix. Moreover, dolomitic powder is a standard construction material with fixed grain-size composition (particle content in size up to 0,071 µm is not less than 80–85%). Experimental research has been conducted on the localities and storm run-off purification based on the filtration of the oily waste water through the dolomitic powder under high pressure (6–8 atm.)

The determination of oil concentration in the storm water illustrates that such waters are specified by significant difference in the pollutant concentrations. Under sample 1 purification oil concentration decreased from 23.49 to 1.06 ppm. Under sample 2 filtration water treatment was ineffective because of the initially low oil concentration (0.85 ppm). At the oil concentration of 0.85 ppm it's content in the purified water increased to 0.93 ppm. It can be explained by the fact that even dolomitic powder whilst grinding can soak a quantity of oil from lubrication fluid of production equipment. In light of the foregoing it is fair to say that dolomitic powder is an advanced absorbant for the localities of storm water purification from petroleum products.

According to the results of research, it is evident that the possibility in principle of reductions in the toxicity of high concentrated oily waters by sorption of contaminants on the mineral sorbent – dolomitic powder.

The optimization of engineering aspects of suggested method under future research will allow it's effective implementation to the manufacturing process with following reclamation of waste sorbent as a construction material.

NEUTRALIZATION OF ACID TAR WITH SALT OF WATER DEMINERALIZATION

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The method of neutralization with mineral slurry (salts) of demineralizer with water softening equipment is proposed like the most effective method of neutralizing the acid sludge.

The process of neutralization of the acid sludge is supposed to be carried out in the reactor of an original and simple construction which consists of two coaxially arranged tubes. The reactor doesn’t have specific and thermostatic mixing devices. The flow of the acid sludge is entered into the tube of smaller diameter at a rate which can provide the turbulent character of the process. Through the hole of the inner tube acid sludge is got into the outer tube which also got an aqueous suspension of water treatment slurry. Microscopic diameter of the particles of slurry provides a complete interaction between the slurry and a sulfuric acid contained in the acid sladge.

The absence of hydroxides of calcium, magnesium and iron and calcium carbonate as well as neutral environment of the aqueous phase (pH = 7) indicate that the process of neutralization of the acid sludge with mineral slurry can be carried out. Since these sulfates are non-toxic, they can be used in the construction industry: as an additive to concrete, asphalt, as well as serve as a recultivating material for the liquidation of soil pit at the various industrial facilities.

The advantage of this method of neutralization is the fact that the sludge particles have a microscopic size that makes it possible to maintain the suspension of the sludge suspended in the aqueous medium and allows to operate the process in a turbulent flow in the reactor of a simple construction. It should be borne in mind that the implementation of the reaction in the liquid phase with the great quantity of water can solve some technical problems:

- reducing the viscosity of the acid sludge and facilitation of the process of neutralization
- removing the heat of reaction due to high heat capacity of water and significant latent heat of vaporization
- separating the organic phase presenting in the acid sludge from inorganic
- getting a neutralized product, not contaminated with organic substances.

INTEGRATED SYSTEM FOR PRODUCING SLUDGE WASTE BASED ON GROUND COMPOSITES

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Activities of fuel and energy complexes (FEC) is accompanied by the formation of low-hazard waste.

Directions of processing, recovery and recycling of waste at FEC are well-known. They are mainly associated with the production of building materials and secondary reagents for wastewater treatment [1]. However, high energy costs and material costs hinder their implementation. As a result, the waste at FEC are deposited in a storage.

Promising direction of waste utilization at FEC is their use as composite remediation materials for the restoration of disturbed lands. These materials are composites based on waste subjected to a pretreatment in order to reduce volume and toxicity . Directions of waste utilization include the use of waste composites for vertical planning, lifting of hypsometric marks of recesses, technical and biological screening of storages, formation of closure embankment, wedges of slope flattening, ground for technological roads [2].

Production of composite materials based on remediation of waste is associated with the need to process them. However, not all waste at FEC can be used as a remediation material as well as not all degraded land can be reclaimed using expose waste. Development of an integrated system of waste compliance to the directions of their using is required.The basis of the proposed system is the principle of phase selection on certain criteria, principles of achieving natural similarity to disordered geo-environment and separating approach of dominant components of the composite.

Taking into account the basic principles the research on waste management into composite materials remediation at FEC was conducted.T heir production included three processes: dehydration, confusion and consolidation.

Using composites on the basis of waste at FEC was applied in the preparation of areas disturbed by object dismantling of inactive buildings and enterprises installations in the Samara region. The economic effect of the developed technologies is achieved by reducing the required volumes of natural soil and return of the recovered territories in economic use.

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ALTERNATIVE DIRECTIONS OF DRILLING WASTE TREATMENT

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During the drilling and operation of oil wells large-tonnage drilling wastes with an initial moisture content to 98.0% are produced . They are particles of drill cuttings suspended in the volume of waste drilling mud. Depending on drilling mud composition hazardous waste class may vary from 3 to 5.

The goal of drilling waste treatment is to reduce their volume and create the transportable, sanitary and safe material suitable for recycling. To achieve the goal drilling waste must be subjected to dehydration (removal of excess water) followed by consolidation.

Existing methods of drilling waste dehydration involve two main groups: natural waste treatment and forced waste treatment.

Natural waste treatment methods include technologies that use gravity and natural evaporation processes (no any artificially introduced processes). Hardware design methods of natural treatment is simple in construction with lack of moving parts.

Forced waste treatment include mechanical and thermal effects by placement of drilling wastes in special units (centrifuges, filters, furnaces, dryers). Processing time of forced waste treatment is much less than natural waste treatment, but the capital and resource costs disproportionately large compared to natural waste treatment.

In the context of the oil-producing fields it is reasonable to combine both groups of treatment . The combination of these techniques in a single processing unit is suitable for the area of improvement sludge pits. In this case it is possible to implement certain points of the pitless drilling concept.

An alternative method of drilling waste treatment is their neutralization using filter textile shells (FTS-method). This method was developed by «TenCate Geosynthetics Netherlands bv» (Netherlands) and became popular in the late 90s of the twentieth century. In the Russian Federation FTS-method was introduced in 2005 by JSC "Admir Eurasia" (Moscow).

Processing by FTS-method is forced waste injection into a textile flexible containers based on polymeric membranes of unipolar conductivity. Waste dewatering reaches moisture content 55,0–65,0% from 98,0–99,0 after filling the container using gravity and capillary force of liquid absorption into interporous space. Container processing feature is that filtering happens through a filter cake layer and through the filter membrane. Depending on the characteristics of the filtration and process conditions the residence time of waste lot in the shell ranges from a few days to a year or more.

The main feature of container treatment method compared to existing methods is that the filtering processes and waste compaction happen in a single unit.

DIRECTION OF BIODIESEL PRODUCTION WASTE TO PRODUCE THE PLASTICIZER FOR THE POLYMER COMPOSITIONS

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Currently the world volumes of biodiesel production are more than 20 million tons per year. For every tonne of prodused biofuel about 100 kg of waste is coming out. This waste is named as Glycerol-based Fraction. In frames of this situation the problem of utilization of this by-product is very serious. Moreover such glycerol is contaminated with methanol, potassium hydroxide and salts of fatty acids. Therefore using of this raw material in area of chemical industry is greatly hindered.

This paper contains some proposal of glycerol-waste reclaim to get finally such an important and valuable product for the polymer industry as a plasticizer.

Today all suppliment and consumption of plasticizers for Russian and aspecially for international market is strongly depends of the environmental, human health protection and other legislation. According to conducted expertise all products made from PVC and containing dioctylphthalate are harmful to human health. So now the production and sailing of children's toys made using this materials are strictly prohibited. Therefore manufacturers are actively seeking a plasticizer that would satisfy all the technical requirements and would be environmentally safe.

As the plasticizers substances such as esters of glycerol may be successfully used. It can be even a glycerol derived from biodiesel waste.

In this work we have investigated the possibility of synthesis of glycerol esters from biodiesel waste as a starting material. Experimentally we have found the most appropriate for this purpose carboxylic acid. The optimal industrial synthesis conditions has been also recommended. The kinetic parameters of the process and principal technological scheme of plasticizer production were additionally determined. Physicochemical properties (viscosity, flash point, volatility) were shown and the plasticizing properties of obtained product were completeley proved.

Industrial trials are implemented on the production site "Tarkett" - the largest producer of floor coverage. According to testing results all submitted samples are fully satisfy of all requirements applied to the plasticizer compositions. Finaly our formulations are recommended as a fine component of PVC compounds.

We have obtained patent documents for the declared plasticizer. So at the moment all rights reserved. All propreties of obtained plasticizer in this work were compared with other plasticizers. In many ways it is superior to all competitors.

PROBLEMS OF WASTE STORAGE DECOMMISSIONING AT GAS AND OIL COMPLEXES USING AERATION PLANTS

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Activities of oil and gas companies are accompanied by the formation of liquid and tabular. hydrocarbon waste.

A common way of dealing with these types of wastes is their placement, storage in specially equipped facilities (sludge reservoirs, ponds, anaerobic digestion, etc., hereinafter reservoirs).

Storage decommissioning requires creating of specialized complexes composed of mechanical and biochemical processing of hydrocarbon-containing waste with subsequent production of remediation materials.

Figure 1 presents schematic interaction diagram of geo-ecological system elements in storage decommissioning technology with hydrocarbon-containing wastes using enterprises formed on the basis of the redeveloped aeration plants.

The proposed technology of storage decommissioning has been developed on the basis of reconstructed treatment facilities of JSC "Novokuibyshevsk Petrochemical Company" Samara, Russia. Additional processing units of water-based emulsion layer treatment, bottom sludge treatment and excessive film of the bioreactor were introduced into the current scheme of the investigated aeration plant. Facilities of inactive sections of aerotanks are proposed to reconstruct to combined bioreactor [1].

There is a significant number of storages and aeration plants in oil and gas recovery fields.

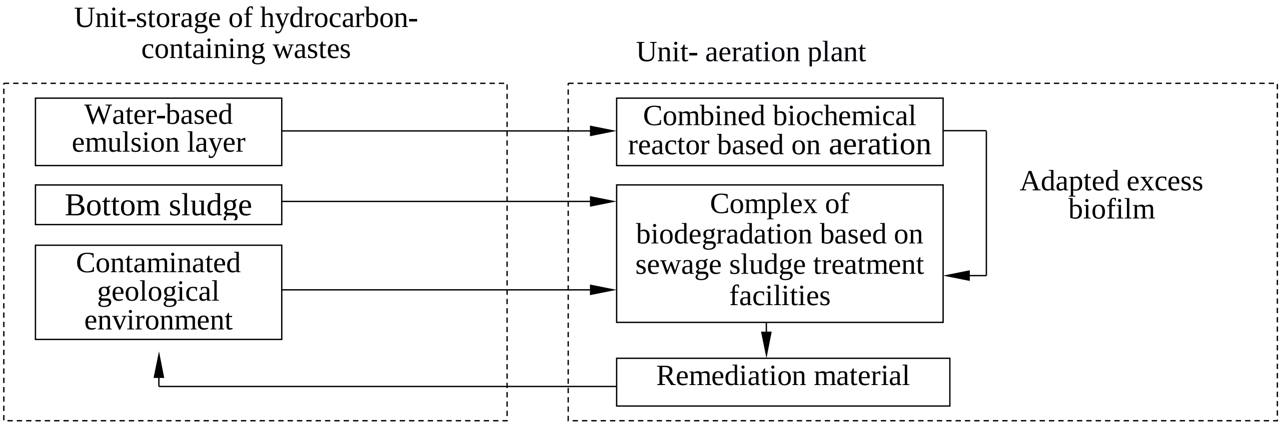

Figure 1. Schematic interaction diagram of geo-ecological system elements “reclaimed storage - aeration plants”.

However, there are no unified data that determine the possibility of application of proposed storage decommissioning technology at aeration plants . Assessment of capability for reconstruction of aeration plant for hetero- waste storage treatment are recommended to implement by sequential sampling using groups of related technical, resource and economic criteria corresponding to the stages of selection.

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DECOMMISSIONING FEATURES OF UNAUTHORIZED LANDFILL FACILITIES AT SPNA

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The old objects of organo-mineral waste disposal – landfills and reservoirs – remain dangerous for ecosystems. Some of these objects were formed on flooding, landslides and karst areas, as well as in protected areas in close proximity to residential areas.

The need to restore the disturbed areas has led to the emergence of various technologies of organo-mineral waste landfill processing [1]. Thus, as a rule, the whole waste landfill is processed array excluding the natural assimilation of the individual fragments in prolonged contact with the environment. Significant amounts of work when exposed to the entire thickness of the landfill soil, discontinuity of already assimilated fragments are responsible for increasing of reclamation costs and lead to secondary pollution of geo-environment.

Minimizing costs and environmental costs can be possible in case of integrated approach to recovery areas. In this case you must consider the special aspects landfills, the presence of non-uniform fragments, coefficient of non-uniformity and the depth of the natural assimilation during long-term placement.

The authors propose the basic principles and technological approaches to the restoration of areas disturbed by waste disposal:

- differentiation of field disturbance on the basic components with the release of fragments of non-uniform structure and properties;
- providing conditions of similarity in composition and properties of basic components;
- maximum use of the resource potential of the object and the territory.

Basic principles presented here have been used for conditions and remediation methodology of landfill assessment in Zhigulyovsk (Samara region.).

The object of the research was operated from 1973 to 2010 in the specially protected natural area (SPNA) – National Park "Samara Bend". This encumbrance complicates any economic activity within the boundaries of protected areas, except for recreation.

Using basic principles and technological approaches made it possible to carry out reclamation project in Zhygulevsk by creating compact landfills having continuity and geomechanical stability.

Basic principles allow to determine the nature of the controlled impact on waste disposal,to minimize masses of remediation materials of natural origin, and develop cost-effective methods of disturbed area restoration with minimal impact on the environment.

Reference:

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DEVELOPMENT OF THE RECYCLING PROCESS OF PULP AND PAPER MILLS CONTAINMENT PONDS

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One of the objectives of the chemical industry is the development of resource and energy saving technologies for processing of harmful industrial wastes, which are inevitably formed even at the most modern enterprises with most advanced technological processes. Such waste may include sludge-lignin wastes, which are present at almost all pulp and paper mills (PPM) in Russia. The problem of their disposal has not yet been solved and a large part of lignin sludge is discharged into containment ponds. Preliminary research, conducted by the authors of the present work, established that the sludge-lignin wastes, produced at different pulp and paper mills of the Russian Federation contain natural lignin, a large set of saturated carboxylic acids of normal and branched structure, consisting from 6 to 20 or more carbon atoms, unsaturated carboxylic acids of olefinic (C_{10} - C_{24}) and acetylene series, hydroxy- and keto- acids, dibasic and alicyclic compounds, sterols and terpenes, waxes and cyclic compounds of rosin and their derivatives, cerols – basic ethers of higher alcohols and many other components, combined in groups of simple, complex and cyclic lipids. From all of these impurities, sludge-lignin wastes are easily separated by methods of sedimentation, filtration, centrifugation, however the separation of the remaining mixture of natural hydrocarbons has certain difficulties. The presence of water, fat acids, resin acids, unsaponifiable matters and lignin, as it turned out, promotes the formation of strong emulsion that is difficult to stratify. In the course of further research, it was established that the natural lignin because of its peculiar properties was kind of "enveloping" the drops of oil such that quite strong and sustainable system was formed, which was difficult to separate and even after heating and curing at the temperature close to 100ºC it was stratified rather slowly.

In this respect, further research was aimed at the search of simple and accessible methods of destruction of stable emulsion and extraction of separate components, the most valuable of which were lignin and raw tall oil. Both of these products are commercial, and are produced by pulp and paper mills as well as by hydrolytic plants. To extract lignin and crude tall oil from LCW emulsion at the first stage of the research it was tested the method of using different solvents of aliphatic as well as aromatic nature, and also widely used in industry: DMFA, DMSO, furfural, crude oil solvent and turpentine. In the result of studies it was found that aliphatic solvents, because of similar molecular structure mainly dissolve the components of crude tall oil – fatty acids, and relatively poorly dissolve lignin, however they show low selectivity. Overall, demonstrated LCW processing method was concluded to be non satisfactory, as it could not meet the requirements due to difficulty in subsequent removal of the solvent from the extract. At the second stage of the research the way of LCW processing by saponification of fat and resin acids of crude tall oil in the composition of LCW with alkaline solutions (NaOH) was considered. During the works the following was determined: NaOH solutions concentrations and their molar ratio with LCW, temperature regimes of the process operation, process hardware design has been studied. The originality of the proposed method of LCW processing by saponification was in the fact that during its usage such tall soaps are formed in the presence of which the viscosity of the system is sharply reduced. While doing this the system "oil - lignin" is quickly destroyed, and the latter, not reacting with alkali, is extracted in the form of suspended mixture (slurry). In such a tall soap the suspended mixture of lignin was easy to separate from other hydrocarbons by filtering or by centrifugal separation.In case of sedimentation of too fine suspended mixture it was tested the method of desalting (electrolytic coagulation) of lignin by adding a solution of electrolyte (NaCl). The study of electrolytic coagulation of lignin from tall soaps gave satisfactory results. The output of lignin during the filtration of soap solution increased by 20–30% in comparison with the literature data.

PROBLEMS OF RESEARCH AND DEVELOPMENT OF NATURAL AND MAN-MADE SYSTEMS

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Economic activity leads to the formation of natural and man-made systems (NMS), composed of man-made structures and natural components geosphere shells, exposed and developed in time and space as a whole. A wide variety of research methods and directions of development of the territories occupied by the NMS are known. Common drawbacks of the known methods are the high cost, the local technical result, satisfaction with departmental interests. Resource and geo-ecological features of industrial cluster, as the main source of generation of NMS are not considered. More over, information on structure, composition, formation and genesis of the life cycle of man-made structures are not considered either. As a result, the latter even after the recent restoration of production continue to have a negative impact on the components of geomedium and rregenerated area is not used anymore.

A complex system of research and assessment of the condition under uncertainty structure, composition and origin of formation will solve development of NMS with least costs. In this regard the comprehensive theoretical and experimental study of NMS with the establishment of the state of its corresponding allocation of life-cycle stages and development directions and methods of recovery and development of the target area seems to be relevant. The latter is difficult due to the absence of theoretical positions and methodological procedures for the assessment of NMS in various areas of development. The basic tenets of the theory and methodology of assessment of NMS as binary systems are presented:

A combination of natural, graphical and numerical methods of research;

- Structural matrix analysis to the interpretation of the NMS as data sets and three-dimensional models and recovering heterogeneous fragments using principal component analysis;

- Assignment of NMS to the selected stage of the life cycle using characteristics groups of space-time assessment of positioning, structural organization and the potential ability to be recycled ;

- Age assessment and stability of man-made mineral formation by indicating its ability to transform the method of biodegradation;

- Logistical analysis of NMS and evaluation of their recycled abilities.

Developed theoretical positions and assessment methodology of NMS as binary systems allow to make science-based technologies of managed recovery with minimal impact on the natural geological environment. In particular, the basic principles form the basis for new technologies of managed impact on NMS: aggregation technology geo-container processing sludge, conversion technologies of processing of hydrocarbon man-made structures, liquid storage technogenic formations using aeration stations, inoculation of array of municipal solid waste.

WAYS TO REDUCE EMISSIONS OF TOXIC COMPONENTS IN THE RUBBER INDUSTRY

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The modernity of scientific-technical and social-economic development favors the growth of technological environmental impact leading to the degradation of ecosystems and impairment of public health, overuse of natural resources, environmental pollution, accumulation and spread of industrial wastes containing different toxic compounds. One of the promising ways for reduction of the technological environmental impact is conversion of economic mechanism at industrial enterprises. An important sphere of such activity is reduction in the release of toxic compound wastes by conversion to the new environmentally compatible technologies. This work does not consider treatment or recycling of wastes of the rubber-processing industry but it considers prevention of their formation by means of using ecologically less aggressive and toxic ingredients.

Structural features of the dust formed from white black lie in the fact that there are active centers on the surface of white black ultimate particles able to enter into chemical reaction with formation of ecologically hazardous substances and polymerize.

In accordance with researches carried out by us we can say that from natural minerals, zeolite is the most challenging to be used in the rubber-processing industry. It is explained by the fact that zeolite due to its chemical composition and structure possesses by unique properties.

It is supposed that efficiency of surface-active substances to a large extent depends on their hydrophilic-lipophilic adsorbed and form bonds on the phase boundary.

To reduce harmful influence of toxic components, particularly phosphate surface-active substances and white black, we propose to substitute them on more safety.

At Shymkent tire works (Ecoshina), insulating compound IS-21 is used for processing of rubber mixtures. However, this compound possesses by increased foaming capacity, does not provide safety of mixtures without adhesion during long time, causes strong metal corrosion because of reduction in pH medium at storing. Insulating compound also contains phosphate surface-active substances and talc which is also environmentally hazardous and causes human respiratory tract diseases and parasitism. Furthermore, composition of the rubber mixture itself contains white black which toxicity is above mentioned. Proceeding from this we have carried out researches on possibility to substitute these toxic components. We propose to substitute phosphate surface-active substances on surface-active substances synthesized from the wastes of chemical fibers (TEAPAN).

The researches on possibility to use surface-active substances TEAPAN in the base of insulating compounds have produces positive results. Insulating compounds were prepared by mechanical mixing in laboratory electric mixer. Therefore,on the basis of the proposed SAS - "TEAPAN" developed environmentally friendly insulating compounds with low foaming, best adhesive properties that can reliably prevent sheets from sticking together rubber mixtures. Developed insulating compounds also have inhibiting properties in relation to metals that is explained by preservation of alkali medium during long time. Using of zeolite instead of talc also allows improve labor conditions and ecology.

Also we used new synthesized surface-active substances for improvement of surface activity of zeolites applied as mineral fillers in rubber mixtures instead of toxic white black. The research results showed perspective of using of modified surface-active substances of zeolite: mechanical strength characteristics of tire rubber have been improved. Researches in the given direction will be continued.

ON THE PROBLEM OF PROCESSING PHOSPHOGYPSUM

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Phosphogypsum produced as waste in factories, processing apatite by sulfuric acid technology. Currently accumulated millions of tons of phosphogypsum representing undoubted, environmental hazard due to the presence of fluorine compounds, which can be transported in the form of dust particles over long distances. At the same time, phosphogypsum can be a source of rare earth elements (REE), the contents of which reaches 0.3–0.5 wt %.Various methods proposed for the disposal of phosphogypsum, providing, for example, the complete decomposition of phosphogypsum by sodium carbonate [1] or receiving gypsum – cementitious materials [2], and as a byproduct – concentrates of rare earth materials. However, they did not find practical application and phosphogypsum dumps continue to increase. The lack of progress on this issue, perhaps due to the fact, that the waste phosphogypsum treated as an independent raw material without any connection with the main production.

The processing costs are excessive for this reason. The main problem is that sulfuric acid need to clean phosphogypsum in such an amount, that its costs and disposal costs exceed the value of the selected rare earth. The author has found a solution within the existing main production technology. As is known, opening of apatite with sulfuric acid is carried out in continuous mode processing apatite to obtain phosphogypsum and phosphoric acid. It is proposed to conduct the reverse process, i.e. to neutralize the excess sulfuric acid generated during purification of phosphogypsum from fluoride and phosphate - ions.

$$5H_2SO_4 + Ca_5F(PO_4)_3 = 5CaSO_4 + 3H_3PO_4 + HF$$
$$Ln_2(SO_4)_3 + 6NH_4OH = 2Ln\,(OH)_3 + 3\,(NH_4)_2SO_4$$

Phosphogypsum resulting return to the head of (5–7% of the amount of the primary), concentrate hydrated- phosphate REE isolated from the solution, and ammonium phosphate solution is routed to the main washing phosphogypsum production. The main processing parameters phosphogypsum sulfuric acid for removal of phosphorus and fluorine, the treatment conditions by sulfuric acid solutions apatite, allocation parameters lanthanide concentrate (10–15%) from solution have been defined in the neutralization of ammonia. Preliminary technical – economic calculations have shown, that this technology utilization of phosphogypsum can be economically justified, because in this case:

1. Costs for reagents recouped the cost of REE and allocated an additional amount apatite of processing to obtain phosphate salts.

2. The entire mass of the output process of phosphogypsum not contain harmful impurities and does not constitute environmental hazards.

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VEGETABLE OIL AS FUTURE OF A “GREEN” CHEMICAL TECHNOLOGY

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Due to the new legislative regulation of the fuels quality, a more attention of the world scientific community has been focused on using biomass as a source of energy.

170 billions metric tons of biomass are produced per year by photosynthesis, 75% of which can be assigned to the class of carbohydrates. Only 3–4% of these compounds are used by humans for food and non-food purposes [1]. A vegetable oil can be one of the most prospective products of biomass.

There are different ways of using of this resource. One of them is a production of biofuels. Biodiesel is the methyl or ethyl esters of fatty acids. The process of its production is based on a reaction of oil’s transesterification with corresponding alcohols. In the last few years a lot of publications have dealt with the way of the improving of this production. Even more, a hydrogenation of esters of unsaturated acids were proposed in the work [2] in order to obtain saturated esters and alkanes, which can be used for a preparation of washing agents.

Other useful component of vegetable oils is the glycerol, that is a byproduct of the biofuel production. The increase of the biofuel production has led to the dramatic decrease of a glycerol price. Today a very important aim is to find optimal methods of valorization of this glycerol. Our research group has proposed two methods of using of the glycerol. The first is the esterification of glycerol with carboxylic acid in order to obtain a plasticizing agent for PVC-compositions.

In this work we have considered the second proposed way of the glycerol valorization by synthesis of ethers of the glycerol and linear and branched out alcohols. The method of preparation of glycerol ethers was elaborated in the course of the works. The samples were synthesized and purified, and physical parameters, such as an enthalpy of vaporization and a vapor pressure, were determined during this investigation. As we think, obtained compounds can be used as prospective fuel additives, because they have a low vapor pressure and a high content of oxygen’s atoms in the molecule.

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INDIRECT ELECTROCHEMICAL OXIDATION OF ORGANIC COMPOUNDS

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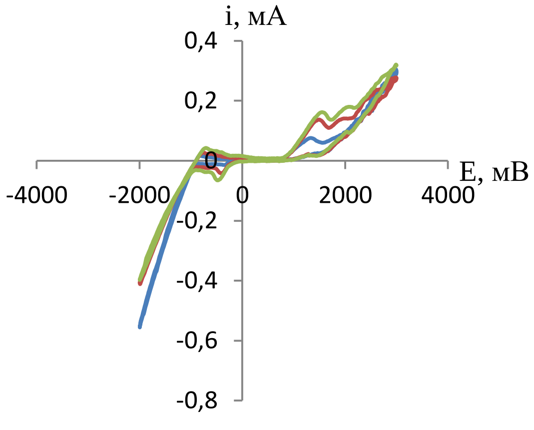
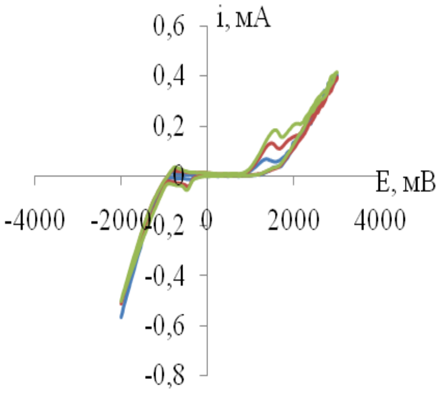
Nowdays the phenol chemical compounds of an antrachinonovy row are widely used in industry [1]. They are used, for example, as raw materials to produce tires, rubbers and antiseptics. It leads to pollution of industrial drains by hardly oxidized organic compounds, and it is not easy to treat them due to the structure of these compounds. That is why appeared the interest to the development of ecologically pure methods to treat them. Especially to the methods based on the electrochemical oxidized processes. Among them the most effective is indirect electrochemical oxidizing method which allows to generate in situ the active oxygen forms as intermediated $OH^{\cdot}$, $HO_2^{\cdot}$ and HO_2^-, which leads to mineralization of the organic compounds till the water and carbon dioxide [2]. The effectivity of the electrochemical treatment of the industrial wastewater depends on the electrolyzer configuration, content and geometry of electrodic materials, the currents density and the characteristics of environment [3].

In this work we investigate the treatment of the wastewater simulators containing 1,3-dioxibenzol and 1,2-dioxiantrachinon-3sulfonic acid of sodium salt by indirect electrochemical treatment in the coaxial diaphragm less electrolyzer. The transformation of the organic compounds is estimated by the cyclic voltamperometry and absorbing spectroscopy methods. It is stated that the compounds do not react on the electrodes. It is proved by the cycled voltampermetry curves recorded in background solution with organic compounds. Moreover, it is stated that the concentration does not influence on the electrode process. But the concentration of the free alkaline, on the contrary, influences on the result of the transformation of the organic compounds in the reactor volume. It is seen in the absorption spectrums of the treated solution. Their maximums decay by the time. It allows to conclude the degeneration of the organic compounds during the indirect oxidation by the metastable electro generated reagents as HO_2^-, $OH^{\cdot}$, $HO_2^{\cdot}$.



(a)



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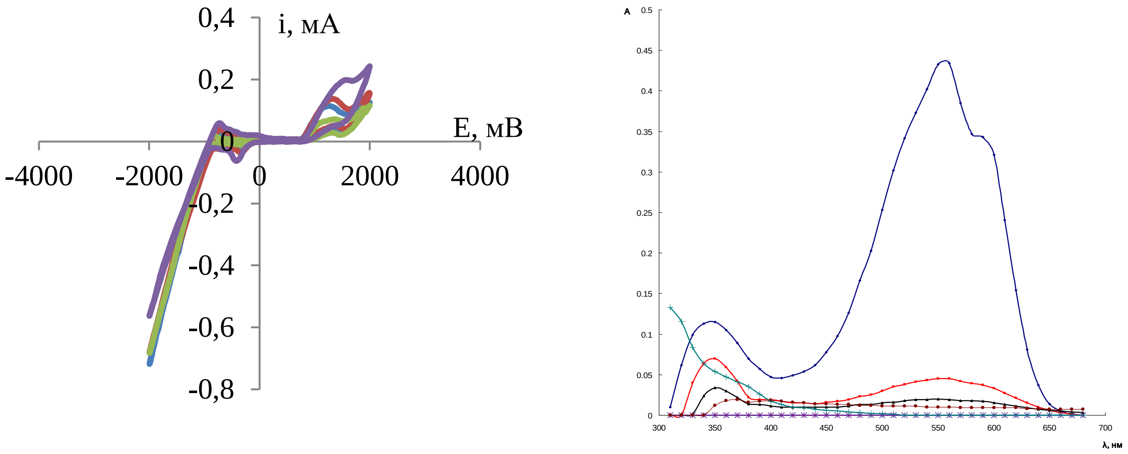

(c) (d)

Figure. 1 Voltampermetry cyclic on platinum electrode: a – 0.01 M NaOH, speed of development of potential: 1 – 10, 2 – 20, 3 – 100 mV/s; б - 0.01M NaOH + 1,3- dioxibenzol, speed of development of potential: 1 – 10, 2 – 20, 3 – 100 mV/s; в – 0.01 M NaOH + 1,2-dioxiantrachinon-3sulfonic acid of sodium salt (0.01gl^{-1}), speed of development of potential: 1 – 10, 2 – 25, 3 – 50, 4 – 100 mV/s; г – spectrum of adsorption of solution 1,2-dioxiantrachinon-3sulfonic acid of sodium salt (10^{-2} gl^{-1}) в NaOH (0.01 M), electrolysis time τ, min (1 – 0; 2 – 30; 3 – 60; 4 – 90; 5 – 120; 6 – 150; 7 – 180).

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